

Development of A Test For Water-In-Oil Emulsion Breakers

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Environment Canada and the U.S. Minerals Management Service have conducted studies on the breaking of water-in-oil emulsions over the past five years. These studies have three trusts: first to develop a standard test for the emulsion breaking agents; second to test commercial products on the market; and thirdly to understand the physics of emulsions. Nine basic types of shaker/test methods were tried over the years. Although results are comparable with different tests, a stable water-in-oil emulsion must be used to yield repeatable results. Tests with unstable emulsions will show unrepeatable and inconsistent results. The factors for testing emulsions are as follows:

1. Stability of the emulsion - emulsions must be stable to yield consistent and repeatable results, this is easily achieved using a known emulsion-producing oil in a high energy device
2. Energy in the test vessel - breaking of an emulsion requires some energy. The energy is variable with different types of agents, some agents will not break an emulsion without energy. There is a time-energy trade-off as well. The type of energy induction be it rotation or shaking does not appear to have an effect.
3. End-point test method - We have tested a variety of test measures but have primarily focussed on water content by Karl-Fischer titration and viscosity. It has been found that a loss of water as low as 10% can result in the breaking of an emulsion. The presence of large water droplets in a "broken" emulsion makes water-content methodology noisy. After breaking, all emulsions form a "foam-like" substance along with black oil. Measuring the viscosity of the emulsion is a more consistent method, however this requires an expensive plate-plate viscometer.
4. Oil-to-water ratio - The oil-to-water ratio in the test vessel is important in order to yield correct results. Many agents are water-soluble and when the oil-to-water ratio is large, such as at sea, these agents are much less effective than those that are not water-soluble. A minimum ratio of 1:300 is required to differentiate these products. A ratio of greater than 1:500 is suggested.
5. Mixing time - The mixing time required to yield a result is variable with the type of agent. A minimum of one hour has been found necessary to reduce noise. Most tests show no additional increase in agent effectiveness after three hours.
6. Settling time/post-treatment - After the emulsion is broken, a foam-like material remains. This material usually contains large un-incorporated water droplets. These must be removed before testing for either water content or by viscosity. Settling of about 15 minutes or more is marginally effective, however centrifuge treatment is best.

7. Treatment ratio - Most agents are operative from 1:100 down to about 1:500, agent to emulsion ratio. These values can be repeated for a given emulsion with a specific test and agent.

Several agents were tested for effectiveness. Recent work was done using the product Alcopol 60, a water-soluble sulphosuccinate, and the Environment Canada product, now called Vytac DM. Both products are effective at breaking oil-in-water emulsions. Alcopol is less effective as the oil-to-water ratio is increased. Vytac DM operates at ratios as low as 1:2000 (agent to emulsion ratio).

PHYSICS OF EMULSIFICATION

Emulsification is the process of the formation of water-in-oil emulsions often called "chocolate mousse" or "mousse" among oil spill workers. These emulsions change the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 50 and 80% water thus expanding the volume of spilled material from 2 to 5 times the original volume. The density of the resulting emulsion can be as great as 1.03 g/mL compared to a starting density as low as 0.80 g/mL. Most significantly, the viscosity of the oil typically changes from a few hundred cSt to about one hundred thousand cSt, a typical increase of 1000. This changes a liquid product to a heavy, semi-solid material. Emulsification is felt by many to be the second most important behavioral characteristic after evaporation. Emulsification has a very large effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation slows by orders-of-magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also has significant effects on other spill aspects; spill countermeasures are quite different for emulsions. Emulsions are hard to recover mechanically, treat or burn.

The mechanism and dynamics of emulsification have been poorly understood. It was not recognized until recently that the basics of water-in-oil emulsification were understood in the surfactant industry, but not in the oil spill industry. Berridge and co-workers were the first to describe emulsification in detail and measure several physical properties (Berridge et. al., 1968). Berridge described the emulsions as forming because of asphaltene and resin content. Workers in the 1970's concluded that emulsification occurred primarily with increased turbulence or mixing energy (Haegh and Ellingston, 1977; Wang and Huang, 1979). Composition of the oil was not felt to be a major factor. Some workers speculated that particulate matter in the oil may be a factor and others suggested it was viscosity. Evidence could be found for and against all these hypothesis. Twardus studied emulsions in 1980 and found that emulsion formation might be correlated with oil composition. Asphaltenes and metal porphyrins were suggested as contributing to emulsion stability. Bridie and coworkers studied emulsions in the same year and proposed that the asphaltenes and waxes stabilized water-in-oil emulsions. The wax and asphaltene content of two test oils correlated with the formation of emulsions in a laboratory test. Mackay and co-workers (Mackay and Zagorski, 1981a, Mackay and Zagorski 1982a, Mackay and Zagorski, 1982b) hypothesized that emulsion stability was due to the formation of a film in oil that resisted water droplet coalescence. The nature of these thin films was not described, but was proposed to be due to the accumulation of certain types of

compounds. Later work lead to the conclusion that the compounds were asphaltenes and waxes. A standard procedure for making emulsions and measuring stability was devised.

Thingstand and Pengerud (1983) conducted photooxidation experiments and found that photooxidized oil formed emulsions. Nesterova and co-workers studied emulsion formation and concluded that it was strongly correlated with both the asphaltene and tar content of oil and also the salinity of the water with which it was formed (Nesterova et. al., 1983). Mackay and Novak (1984, Mackay, 1984) studied emulsions and found that stable emulsions had low conductivity and therefore a continuous phase of oil. Stability was discussed and proposed to be a function of oil composition, particularly waxes and asphaltenes. It was proposed that a water droplet could be stabilized by waxes, asphaltenes or a combination of both. Viscosity of the resulting emulsions was correlated with water content. Later work by the same group reported examination of Russian hypotheses that emulsions are stabilized by colloidal particles which gather at the oil-water interface and may combine to form a near-solid barrier that resists deformation and thus water-water coalescence (Stiver et. al., 1983). These particles, it was said, could be mineral, wax crystals, aggregates of tar and asphaltenes or mixtures of these. Asphaltenes were felt to be the most important of these particles and controlled the formation of all particles. A formation equation relating the asphaltene, paraffin, aromatic and silica gel (resin) content was proposed. This was later shown to be a poor predictor of oil emulsion tendencies.

Desmaison and co-workers conducted studies on Arabian crudes and noted that emulsion formation was correlated with two factors, photooxidation exposure and amount of asphaltenes (Desmaison et.al. 1984). The photooxidation was found to occur on the aromatic fractions of the oil. Asphaltenes were found to become structured with time and this was associated with emulsion formation. Miyahara (1985) reported that the stability of emulsions was primarily controlled by the composition of the oil, specifically that which resided in the hexane-insoluble fraction of the oil. He did not define what this content was. Miyahara also reported that salt and freshwater emulsions showed relatively similar stabilities, although in one case the salt water emulsion appeared to be more stable. Payne and Philips reviewed the subject in detail and reported on their own experiments of emulsification with Alaskan crudes in the presence and absence of ice (Payne and Philips, 1985). Their studies also found that emulsion formation would occur in an ice field, thus indicating that there was sufficient energy in this environment and that the process could occur at relatively low temperatures.

Environment Canada conducted a series of studies which focussed on the physics of emulsion formation (Bobra, 1992). This study provided experimental results that show, rather conclusively, that emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. The latter are similar compounds and both behave like surfactants when they are not in solution. The aromatic components of oil solubilize asphaltene and polar compounds. When there are insufficient amounts of these components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. These studies are confirmed by a large number of similar studies in the surfactant sciences.

EXPERIMENTAL METHOD DEVELOPMENT

Development of a test method began in 1988. Successive tests were developed to solve problems noted with earlier tests. Tests had to satisfy several criteria:

- the tests had to have a high degree of repeatability
- aspects of the method should be analogous to the sea and the practical application of agents
- two tests are always developed simultaneously, these two tests have different vessels and methods of applying energy to the oil-water system but should have similar results
- test results should be repeatable by new staff without extensive training
- the test results should relate to physical understanding of phenomena, and
- the ultimate test should be repeatable by anyone in the world and the apparatus should be available universally.

Nine basic methods and several variations of each were developed. Old methods were abandoned because of difficulties or violations of the above basic rules.

OLDER METHODS

The initial intent was to both form and break the water-in-oil emulsion, "mousse", in the same vessel, using volume as a means of measuring the changes from oil to emulsion and back to oil. Using a graduated cylinder as a mixing vessel, a wrist-action shaker to provide mixing energy, and an excess of salt water, the first work performed was to find a suitable emulsion. Oil mixtures, time of mixing and water-to-oil ratios were factors of variation. Once an emulsion was consistently formed, work on testing de-emulsifying agents began. Quantification of the effectiveness of the additive was taken as the percentage volume difference of the emulsion after mixing. However, difficulties arose in measuring the volume in the graduated cylinder due to the irregular shape of the emulsion, as well as in creating a consistent mixing action due to the formation of a "plug" of emulsion in the cylinder shaft.

To overcome these difficulties, a separatory funnel was substituted in place of the graduated cylinder, thus increasing the surface area of the water. The emulsion no longer caused plugging, and the water could be separated from the emulsion residue. Quantification of effectiveness then became the amount of water liberated from the original emulsion. These changes coincided with a change in the method of forming the emulsion. Rather than forming the mousse in the mixing vessel prior to adding the demulsifier, the emulsion was formed in a separate mixer, allowing for water content analysis of the emulsion. The water liberated in the emulsion breaking test could then be related to the original emulsion.

Other mixers were tried, without improvement. The only other change in this period was to use viscosity as a quantification of emulsion breaking effectiveness, and finally to use water content analysis. A summary of the evolution is given in Methods 1 to 7. Emulsion formation also evolved from the initial stage of mixing in a graduated cylinder. The first alternative used was mixing in a Fleaker jar using a Reax Rotator-Mixer. This method was successful, but took a considerable amount of time. A faster method was found using a Waring CB-6 Blender. The rigour of the mixing allows for rapid emulsification. This is the method now in use.

Method 1 A

Objective: To create a suitable method for testing demulsifiers. Procedure modified as required.

Mixing Apparatus: Burrell Wrist-Action Shaker with finger-grip clamps

Mixing Vessel: 500 mL Graduated Cylinder

Mixing Conditions: 30 mL mousse
400 mL salt water

Energy of Mixing: 3° arc (Initially 2° for 2 hours followed by 1° for 2 hours, but was considered not energetic enough for these conditions) - Variable

Time of Mixing: 2 hours - Variable

Time of Settling: 1 hour (as needed)

Sample Preparation: None.

Measurement of Effectiveness: Volume of Residual Mousse - volume of mousse read from the graduated cylinder; bulky, unbroken mousse is irregular and measured by approximation and/or averaging.

Comments: Advantages - The shaker is easy to use and apparently effective. Six samples may be tested at once.
Problems - Difficult to read volumes of residual mousse where the mousse has not broken down, but maintains a bulky form. Large range of error.

Method 1B

Objective: To create a suitable method for testing demulsifiers. Procedure modified as required.

Changes: Method of measuring effectiveness.

Mixing Apparatus: Burrell Wrist-Action Shaker with finger-grip clamps

Mixing Vessel: 500 mL Graduated Cylinder

Mixing Conditions: 30 mL mousse
400 mL salt water

Energy of Mixing: 3° arc - Variable

Time of Mixing: 2 hours - Variable

Time of Settling: 1 hour (as needed)

Sample Preparation: Pass contents of cylinder through a 500 micron mesh screen, to remove unbroken mousse, into a 500 mL graduated cylinder.

Measurement of Effectiveness: Water Liberated - measure the volume of water under the oil layer in the cylinder.

Comments: Advantages - Easier and more accurate readings of samples containing unbroken mousse.
Problems - Splashing during mixing greatly affects the results.
- Formation of a "plug" of mousse in the cylinder during shaking, leads to variable results.
- Still a large range of error in reading the effectiveness.

Method 2

Objective: To find a mixer suitable for testing Chemical Emulsion Breakers. The procedure will be set according to the requirements of the mixer.

Mixing Apparatus: Eberbach Reciprocating Shaker

Mixing Vessel: Fleaker Jar

Mixing Conditions: 30 mL mousse
400 mL salt water

Energy of Mixing: single speed available

Time of Mixing: 1 hour

Time of Settling: 1 hour, as needed

Measurement of Effectiveness: Residual Mousse Volume and Water Liberated
- see Method 1

Comments: Advantages -

Problems - Shaking is too vigorous and limited to one speed.

- Apparatus not designed to secure this type of mixing vessel.

- Unable to seal securely, leading to increased error due to leakage.

Method 3

Objective: To find a mixer suitable for testing Chemical Emulsion Breakers. The procedure will be set according to the requirements of the mixer.

Mixing Apparatus: Reax Rotator-Mixer

Mixing Vessel: 500 mL Fleaker Jar

Mixing Conditions: 30 mL mousse
400 mL salt water

Energy of Mixing: 65 rpm

Time of Mixing: 2 hours

Time of Settling: 1 hour, as needed

Measurement of Effectiveness: Residual Mousse Volume and Water
Liberated
-see Method 1

Comments: Advantages -

Problems - Unable to seal securely leading to
increased error due to leakage.

Method 4

Objective: To find a mixer suitable for testing Chemical Emulsion Breakers. The procedure will be set according to the requirements of the mixer.

Mixing Apparatus: Glas-Col 3-D Shaker with separatory funnel holders x6

Mixing Vessel: 250 mL Separatory Funnel

Mixing Conditions: 200 mL salt water

Energy of Mixing: Variable

Time of Mixing: Variable

Time of Settling: As needed

Sample Preparation: Separate water from mousse residue

Measurement of Effectiveness: Water Liberated - see Method 1

Comments: Advantages - Able to run 12 samples at once.

Problems - Unable to control speed due to lack of
apparatus consistency.

- Energy of mixing is not identical for all samples.

Method 5

Objective: 1. Improve quantitation of effectiveness.
2. Eliminate mixing problems due to formation of a mousse "plug".
3. Eliminate leakage during mixing.

Mixing Apparatus: Burrell Wrist-Action Shaker with front-mounted separatory funnel holders.

Mixing Vessel: Teflon 1 L Separatory Funnel with screw cap

Mixing Conditions: 60 mL mousse
800 mL salt water

Energy of Mixing: 1 degree arc

Time of Mixing: 2 hours

Time of Settling: As needed to separate layers

Sample Preparation: Separate water off, collect mousse residue

Measurement of Effectiveness: Viscosity on the Haake RV 20 Rotovisco

Changes: Separatory Funnel Advantages - Eliminate mousse "plug" by creating a larger interface during mixing.
- Able to separate water from mousse for testing.
- Eliminates leakage during mixing.
- Mousse has lower tendency to cling to teflon walls.

Problems - Necessitates use of funnel holders not designed for the shaker.

Viscosity Advantages - Quantitative measure of effectiveness with smaller range of error.
Problems - Still not a precise method for assessing effectiveness.

Note - the time of increasing the shear rate was altered at one point without noticeable consequences.

* * Note - four funnel holders were attempted, but were too unstable to use.

Method five resulted in data that was collaborated by later work. The data are presented in Table 1 and graphically in Figure 1. These data show that the emulsion is broken by "Demoussifier" at a ratio of product-to-oil of about 1:1000. These are borne out by later tests. Further development work was conducted to test other methods and to improve on the accuracy of the measure.

Method 6

Objective: Find best method of measuring effectiveness

Mixing Apparatus: Burrell Wrist-Action Shaker with front-mounted separatory funnel holders

Mixing Vessel: Teflon 1 L Separatory Funnel with screw cap

Mixing Conditions: 85 mL mousse
800 mL salt water

Energy of Mixing: 1 degree arc

Time of Mixing: 2 hours

Time of Settling: 20 minutes to 1 hour, as needed

Sample Preparation: Separate water from mousse residue

- Measurement of Effectiveness:*
1. *Water Liberation Volume*
 2. *Viscosity on the Bohlin Visco 88 BV viscometer*
 3. *Water Content by Karl-Fisher titration on the Metrohm 701 KF Titrino titrator*

Comments:

- *All methods quantify the effectiveness of the demulsifier being studied. Water liberated is easiest, yet subject to greater error. Viscosity is more difficult, variable, and difficult to correlate with actual mousse composition. Water content has the best combination of ease, repeatability, and useful data.*

Method 6 was used to measure the effectiveness of the emulsion-breaking products "Demoussifier" and "Alcopol". Test results are given in Tables 2 and 3 and illustrated in Figure 2. Figure 2 shows both the viscosity and water content data on the two products tested. Both tests do show strong breaking points, the water content at about a 15% water loss and viscosity at about a factor of 2. The break for the water content appears sharper. Alcopol and Demoussifier are similar in effectiveness, except that demoussifier shows some effectiveness at ratios as low as 1:2000 (agent to oil), whereas the effect of Alcopol is not seen until about 1:500. Alcopol does, however, apparently move faster to a lower water content at low ratios. The second part of Table 3 shows the effect of placing the treating agent, Demoussifier, directly on the water instead of on the oil. For this agent, this does not have a strong deleterious effect.

A new method was required because the strain on the shakers caused several failures of the shakers. Method 7 is similar to method 6 except that the shaker is substituted with a horizontal holder.

Method 7

Objective: To solve the problem of excessive strain on the Burrell shaker.

Changes: Use Separatory Funnel holders mounted on Top Platform instead of Front Mounts

Mixing Apparatus: Burrell Wrist-Action Shaker with Top Platform
securing 2 large separatory funnel clamps

Mixing Vessel: Teflon 1 L Separatory Funnels

Mixing Conditions: 85 mL mousse 800 mL salt water

Energy of Mixing: 1 degree arc

Time of Mixing: 2 hours

Time of Settling: 40 minutes

Sample Preparation: Separate water from mousse residue

Measurement of Effectiveness: Water Content by Karl-Fisher titration

Comments: Top Platform Advantages - The separatory clamps designed for use with this accessory on the Burrell shaker, eliminating much of the stress on the shaker observed with the holders used previously.

The top platform changes the plane of shaking from vertical to horizontal.

The shaking action observed appears more turbulent, like a wave, rather than a swirl as seen previously. A comparison of the results obtained from the two shaking methods indicates the change in angle has little effect on the effectiveness of the demulsifier. The change in orientation of the separatory funnel greatly reduces the vibration experienced by the shaker.

The latter method was used with several variations to conduct sensitivity studies of the method with varying physical parameters. The method used for these studies is shown in the Appendix.

STUDIES ON THE EMULSION-BREAKING TEST

Once a basic test was established, a series of studies was conducted to examine several basic parameters. The studies under investigation were:

- Shaking Time Studies
- Settling Time Study
- Water to Oil Ratio Study
- Energy Study

The apparatus utilized to provide the energy of mixing in these studies were the Burrell Wrist-Action Shaker (Burrell), and the Turbula T2C Shaker-Mixer (Turbula). The test procedures used for the individual shakers are found in Appendix. The only differences between the procedures are the equipment changes required to adapt to the distinctly different shaking actions. Amendments to these procedures are made dependent on the property under study (eg. time of shaking) while maintaining the integrity of the remainder of the procedure. The changes are noted in the tables or the text where the test results are presented.

The emulsion breakers applied were the Environment Canada Demoussifier (Demoussifier), currently known as Vytac DM and a 60% Alcopol solution (Alcopol). These were used at various ratios of demulsifier to oil (D/O), as noted in the data.

Shaking Time Studies

The purpose of this study was to determine the optimal time of shaking for the test. The intention of the study was to see if a shorter time of shaking could be applied than the two hours previously in use. Initially, times of thirty minutes, one hour and two hours were chosen for study on the Burrell with ECD and Alcopol emulsion breakers. A range of D/O from 1:100 up to 1:1000 was to be used to examine the general trends. However, results showed that this study needed to be expanded to include longer shaking times and larger D/O ratios. A second shaker, the Turbula, was included for comparison.

Burrell

The conclusion reached from the initial study using Demoussifier was that a 2-hour shaking time achieves a sharper break-point than using shorter times, and is therefore more accurate for determining effectiveness. It was later realized that the threshold had not been reached for shaking time effect, and the shaking time was increased to three and four hours. The range of D/O was extended to larger values as the limit had not been determined for emulsion breakdown. At 1:10 (D/O) the trend indicates a threshold is being reached.

The results using Alcopol also show that the 2-hour shaking time increases emulsion breakdown compared to the shorter times. The notable aspect of the Alcopol results is that the water content begins to increase again at a 1:10 D/O. Taking the D/O out to a 1:1 ratio, it appears the water content levels off somewhere between 20% and 40%. The reason for this "J" effect is yet unknown.

Table 4 presents the data from these tests. Figures 3 and 4 show that emulsion breaking is increased as the time increases from 0.5 to 3 hours but after three hours there is no net improvement in the ratio which causes the emulsion to break (by increasing the shaking time).

Turbula

The Turbula shaker was used as a second energy source with a different mixing motion in order to compare the results with that achieved by the Burrell shaker. The first task was to determine the appropriate running speed to best correlate with the Burrell shaker. The three highest speeds were chosen on the Turbula, and compared with the results from the Burrell at 1:100 D/O. By visual inspection, it was decided that fourth gear best-approximated the values obtained from the Burrell, and should be used for comparison. All test results are given in Table 5. Results are depicted graphically in Figures 5 to 8.

The D/O ratios used on the Burrell were tested using the Turbula in fourth gear. At a 2-hour shaking time, differences in data were observed for the Turbula compared to the Burrell. Subsequently, Turbula third gear was used. The results parallel the Burrell. The results of the Burrell and Turbula at third and fourth gears are shown in Graph 6. It may be noted that Turbula fourth gear, 1 hour shaking is virtually identical to that of third gear, 2 hours shaking. Since it is advisable to keep as many factors as possible the same, Turbula third gear with 2 hours shaking, is the best choice for comparing with the Burrell results. Some tests using longer shaking times were tried, and these show no increase in emulsion breaking.

These results show that 2 hours is a satisfactory shaking time for the Turbula mixer, no further increase in emulsion-breaking is observed with longer times.

Settling Time

Time of settling was studied to see if extra settling time could be substituted for time of shaking, thereby reducing demand on the shaker and increasing the number of runs per day. The results for varying settling times are shown in Table 6 and Figure 9. There is little indication that time of settling has any effect on the effectiveness of the demulsifier in the test. However, more results are required to substantiate this conclusion.

Water to Oil Ratio (WOR)

The WOR was studied to establish the appropriate volume of mousse to be used in the test. In previous studies the volume of mousse added to the salt water had been set at 85 ml, giving a WOR of 47. The quantity was chosen to accommodate the minimum oil volume requirement of the viscometer which was then in use. Viscometry is not part of the current test, thus the limitation is not applicable at the moment. The minimum sample volume requirement of the present test, using Karl-Fisher titration to measure water content, is approximately 1 mL of sample.

WOR values from 47 to 500 were chosen for study. The results are shown in Table 7. Figure 10 shows a clear trend toward increased emulsion breakdown for higher WOR values at a 1:1000 D/O. The 1:10 D/O results show a similar trend. This shows that a higher WOR causes a lesser water content in the oil. Subsequent

studies on Alcopol show that this product, which is water soluble decreases in effectiveness substantially at high WOR values. A higher WOR also better approximates the infinite dilution found at sea. However, at a WOR value of 500, it is very difficult to recover sufficient sample for analysis, and introduces a greater potential for residual water to influence results. The WOR value chosen for the test must therefore be less than 500 to provide adequate sample volume for measurement unless a different measurement method is used.

Further study is required to fill the gaps, and to clearly establish trends.

Effect of Energy Level

A study to establish the relationship between energy of shaking and demulsifier effectiveness is perfectly suited to the gear-driven Turbula. The known speeds of the various gears allow for a relationship to be made between energy and effectiveness, if there is one.

The results using the five speeds of the Turbula over 2 hours shaking times, (see Table 8 and Figure 11), show a slight trend toward increased effectiveness with increased energy of mixing. Over the range of energies provided by the Turbula, the effect of increased energy does not appear to be large.

Further study is required to improve the statistical reliability and to include values for which mechanical energy is not imparted to the system (senescence).

RECENT STUDIES

The results provided in this section are those produced since September 1992. Some are continuations of studies begun before; others are new studies initiated to clarify previous work. Work on the formation and stability of emulsions has been included. The procedures for these studies are the same as before, with exceptions as will be noted.

The studies in this section are as follows:

- Shaking Time Studies, Demoussifier, 8 hours
- Settling Time, Alcopol
 - 1:1000 & 1:680 DOR
- Energy Study, Demoussifier
 - Senescence, Demoussifier, Viscosity
 - Senescence, Alcopol
- Post Water Separation Settling Time, Alcopol
- Water to Oil Ratio Study, Alcopol
- Stability Study on Emulsions

The result of these studies has been the change of the standard procedure. The changes include a three-hour shaking time, a 10 minute settling time, and a WOR of 1:200 (20 mL mousse in 800 mL of salt water).

Shaking Time Studies

The shaking time study begun previously using Demoussifier was extended to include 3, 4, 5 and 8 hour shaking times. This was to see if longer times had an effect on the effectiveness of the demulsifier. Table 9 and Figure 12 show the results of these tests. The conclusion is that shaking times beyond 2 hours do effect the

operability of the demulsifier, but times beyond 3 hours do not offer significant advantage. The conclusion is that 3 hours is the optimum shaking time for the effectiveness test.

Settling Time Study

Further settling time studies were performed using Alcopol demulsifier at 1:1000 DOR, then at 1:680 DOR. The 1:1000 runs were performed to confirm that settling time is not a significant factor. The results for these tests are listed in Table 10 and illustrated in Figure 13. While the correlation could not be improved, it is apparent that settling time is not a significant factor. Upon reflection, it was noted the water content of the mousse residues studied were either <20 % or >70 %. These have high probability of being stable mixtures.

Energy Study

Results of further studies on the effect of increasing energy are shown in Table 11 and Figure 14. The data were obtained using the Turbula shaker and Demoussifier. These results show clearly that energy has a strong influence on the operability of the emulsion breaker, at least in this case. The effect of energy is much greater for the Demoussifier than with Alcopol (Alcopol results are given above). This observation has been supported by senescence runs on both Demoussifier and Alcopol. To perform these tests, the written procedures used for Turbula runs were utilized, with the exception that the mousse, water and demulsifier mixture were not put in the shaker, but simply left to stand. All other conditions were left the same, including settling time, with the exception of run time which is shown with the results.

The Demoussifier senescence runs did not produce a change in water content from the original mousse, however a noticeable change in the physical appearance of the mousse did occur. The mousse turned from medium brown to almost black, and became much more fluid. To support this empirical observation, viscosity of the emulsion residue were performed, results are given in Tables 12 to 14. The results show a dramatic drop in viscosity corresponding with increased exposure to Demoussifier. The fact that water content does not drop, coupled with the fact effectiveness increases with mixing energy, indicates Demoussifier requires energy input to remove water from mousse.

On the other hand, Alcopol does not require much energy. Senescence experiments using Alcopol show it to be effective in the absence of mixing energy, while mixing energy has limited effect as noted above.

Water to Oil Ratio Study

This study was conducted on Alcopol to parallel the study on Demoussifier. Previously, the Demoussifier results show a slight increase in effectiveness with increased WOR value. The results of the present study on Alcopol show the opposite effect (see Table 15 and Figure 15).

The reason for this contradiction is the water solubility of the two products. Alcopol is water soluble, and therefore loses effectiveness with the increased dilution of higher WOR values.

Emulsion Stability Study

A study on the stability of emulsions was initiated to identify the regions of instability in the water content spectrum. The test method is to mix oil with water in a Waring blender at a specific ratio of oil-to-water. The water content is measured daily for a week to monitor water content changes. The ratios chosen range from 10% water to emulsion saturation, in increments of 10%. Exact ratios are not easily obtained due to water content of the oil itself, and difficulties in controlling oil volumes transferred. For the 30/70 blend of 30% California Crude API=11.0 and 70% Alberta Sweet Mixed, the water content did not change in any of the emulsions over the 7 days. This oil, the standard for mousse formation used throughout the studies on emulsion breakers, is a very stable emulsion requiring physical or chemical factors to destabilize it. This test also shows that the use of a high energy device such as a blender, results in the formation of a very stable emulsion.

Emulsification of Oils Study

The emulsification of oils was studied to better understand the results of emulsion breakers. The method makes use of the Turbula Shaker-Mixer, a 1 L teflon bottle, 800 mL salt water and 15 mL of oil. The oil and water is mixed for the time noted, then transferred to a separatory funnel for a 30-minute settling time, the water is separated and the water content is measured. The water content is measured again a few days after the run is complete to verify stability. The data produced to date on the standard 30/70 Blend and Iranian Heavy Crude are presented. The highest water contents are often produced with the lowest mixing energy, but instability has been noted with these emulsions. Results are shown in Tables 17 and 18 and illustrated in Figure 16 and 17. These show that the lower-energy device, the Turbula, will often not form stable emulsions. As energy is increased, the emulsions become increasingly stable.

CONCLUSIONS

The series of studies show that a test for emulsion breakers can be developed to yield consistent results. The results are not entirely dependent on the shaking methods or vessels. A number of satisfactory combinations can be developed. The critical factor is the stability of the emulsion being tested. Unstable emulsions will show anomalous results. A second important factor is the type of emulsion breaker being tested. Water-soluble products will apparently change effectiveness as the oil-to-water ratio changes. Some types are somewhat more energy sensitive than others. The third factor is the determination of endpoint. These studies show that both water content and viscosity are useful as endpoint indicators, however, viscosity is more difficult to measure but may be more precise as an end point. The result of emulsion breaking is not usually a water-less oil. A type of foam is produced and the water content of this product ranges between 30 to 50 percent. The large water droplets in this product cause inaccuracies in measurement.

The effect of specific variables are described below:

1. Stability of the emulsion - Emulsions must be stable to yield consistent and repeatable results, this is easily achieved using a known emulsion-producing oil in

a high energy device. Stability can easily be measured by leaving the emulsions sit at room temperatures. Unstable emulsions will be readily detected by simple observation of coloration within a five-day time period. Emulsions formed at low energy are less stable. Some oils will produce stable emulsions at many water contents given that high energy is used.

2. Energy in the test vessel - breaking of the emulsion requires some energy, the energy is variable with different types of agents, some agents will not break an emulsion without energy. There is a time-energy trade-off as well. The type of energy induction, be it rotation or shaking, does not appear to have an effect. Some emulsion breakers require more energy than others. Some emulsion breakers may not break emulsions when no energy is present.

3. End-point test method - A variety of methods were tested but we have primarily focussed on water content by Karl-Fischer titration and viscosity. It has been found that a loss of water as low as 10% can result in the breaking of an emulsion. The presence of large water droplets in a "broken" emulsion makes any water-content methodology noisy. After breaking, all emulsions form a "foam-like" substance along with black oil. The viscosity of the emulsion is a more consistent method, however requires an expensive plate-plate viscometer. Interestingly, the appearance of the product may be a reliable indicator. A reddish product is emulsion and a blackish one is not.

4. Oil-to-water ratio - The oil-to-water ratio in the test vessel is important to yield a correct result for emulsion-breaking agents. Many agents are water-soluble and when the oil-to-water ratio is large, such as at sea, are much less effective than those that are not water-soluble. A minimum ratio of 1:300 is required to differentiate these products. A ratio of greater than 1:500 is suggested.

5. Mixing time - Mixing time to yield a final, stable endpoint, is variable with the type of agent. A minimum of one hour has been found necessary to reduce noise. Most tests show no increase in agent effectiveness after three hours. Mixing times up to eight hours were assessed.

6. Settling time/post-treatment - After the emulsion is broken, a foam-like material remains. This material usually contains large unincorporated water droplets. These must be removed before testing for either water content or by viscometry. Settling of about 15 minutes or more is somewhat effective, however centrifuge treatment is best. More work on separation techniques is required since the presence of the water droplets is felt to be responsible for most of the variation in results.

7. Treatment ratio - Most agents are operative from 1:100 down to about 1:1000, agent-to-oil ratio. This value can be repeated for a given emulsion with a specific test and agent. There is a repeatable ratio for each agent and emulsion type. However, emulsion type is not the most critical variable.

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APPENDIX

Procedure for use with the Burrell Wrist-Action Shaker

1. Place retort stand with ring clamp on top loader balance and insert a clean 1 L teflon separatory funnel. Tare the balance.
2. Fill the separatory funnel with 819.2 g of prepared 3.3% salt water. Tare the balance.
3. Mix the mousse to a uniform consistency by stirring with a spatula. Fill the appropriately sized syringe with mousse and expel the desired mass of mousse (default value is 84.6 g, 85 mL) into the separatory funnel.
4. Place separatory funnel in wooden support stand and repeat steps 1 to 3 for a separatory funnel. Shake the demulsifier and allow to settle to remove the bubbles. Using the appropriately sized micropipette, add desired amount of demulsifier.
5. Apply the demulsifier onto the mousse surface exposed above the water level. Touch the tip of the pipette to the mousse to expel the entire volume. Wipe the tip while plunger is fully extended to clean.
6. Cap the separatory funnels and insert mouth first into the large funnel holders attached to the top platform mounted on the Burrell Wrist-Action shaker. Clamp the funnel above the stopcock using three pronged clamps to secure into place. Be sure the apparatus is at 90 degree angles.
7. Set the timer for the desired time of shaking (default time is 2 hours). Start the shaker and timer simultaneously. Move adjustment arm on the Burrell shaker to a 1 degree arc angle of shaking. Turn off shaker when time expires.
8. Move funnels to the wooden support stand. Set timer to desired time of settling (default time is 40 minutes) and begin countdown.
9. After settling, open the stopcocks and drain off the water portions into 1 L beakers. Discard the water.
10. Allow 15 minutes for the mousse residue to settle.
11. Remove the separatory funnels from the support stand and tip back until the oil is no longer at the stopcock. Remove the stopcock from the bottom of the separatory funnel. Drain any water from the mouth of the funnel, then pour the sample into an adequately sized beaker to contain the amount of sample expected. Swab the sides of the funnel with a rubber policeman to remove any remaining residue adhering to the walls of the funnel.
12. Stir the sample with a 1 cc plastic syringe until the mixture is homogenous.. Draw and expel the mixture several times to get a good sampling. Draw up 0.3 mL of sample.
13. Place a 10 mL cylinder into the microbalance and tare. Insert the syringe tip down into the cylinder. Note the weight in the lab book.
14. Turn on the Karl-Fisher titrator. Fill the reaction vessel with solvent mixture until the electrodes are covered by the liquid. Turn the stirrer on. Adjust to a rate sufficient to form a vortex. Be sure the Karl-Fisher reagent has been titred and titrator is in "KFR" mode. Start the titration procedure to condition the solvent. Press "Start" again to get a prompt for sample size. Inject 0.1 mL of the sample into the reaction vessel and replace cap. When injecting, be certain the

sample falls into the solvent, not onto the vessel wall.

15. Return the 1 mL syringe to the 10 mL cylinder and note the weight in the lab book. Calculate the weight difference and enter this value into the Karl-Fisher titrator. Press "Enter" to begin the titration.

16. At the end of the titration, note the % Water Content in the lab book.

17. Perform 2 titrations per sample, 3 if results are not within 2.5%.

18. Clean the separatory funnels with dichloromethane for next use. Be sure to recycle solvents.

Procedure for use with the Turbula T2C Shaker-Mixer

1. Place 1 L teflon wide-mouthed bottle onto top loader balance and tare.

2. Fill the bottle with 819.2 g of prepared 3.3% salt water. Tare the balance.

3. Mix the mousse to a uniform consistency by stirring with a spatula. Fill a 60 cc plastic syringe with mousse and expel into the bottle. Fill the syringe once again, and expel enough mousse to yield 85 mL of mousse (84.6 g).

4. Shake the demulsifier and allow to settle to remove the bubbles. Using the appropriately sized micropipette, add the desired amount of demulsifier.

5. Apply the demulsifier onto the mousse surface exposed above the water level. Touch the tip of the pipette to the mousse to expel the entire volume. Wipe the tip while plunger is fully extended to clean.

6. Cap the bottle. Fold two sorbent pads in half and wrap around the bottle. Insert into the Turbula basket and secure with the clamp rings.

7. Set the timer for the desired time of shaking (default time is 2 hours). Move drive belt onto desired gear groove. Start the shaker and timer simultaneously. Turn off shaker when time expires.

8. Remove bottle from Turbula basket and empty contents into a separatory funnel on the wooden support stand. Set timer to 40 minutes and begin countdown.

9. After settling, open the stopcock and drain off the water portion into a 1 L beaker. Discard the water.

10. Allow 15 minutes for the mousse residue to settle.

11. Remove the separatory funnel from the support stand and tip back until the oil is no longer at the stopcock. Remove the stopcock from the bottom of the separatory funnel. Drain any water from the mouth of the funnel, then pour the sample into an adequately sized beaker to contain the amount of sample expected. Swab the sides of the funnel with a rubber policeman to remove any remaining residue adhering to the walls of the funnel.

12. Stir the sample with a 1 mL plastic syringe until the mixture is homogenous. Draw and expel the mixture several times to get a good sampling. Draw up 0.3 mL of sample.

13. Place a 10 mL cylinder into the microbalance and tare. Insert the syringe tip down into the cylinder. Note the weight.

14. Turn on the Karl-Fisher titrator. Fill the reaction vessel with solvent mixture until the electrodes are covered by the liquid. Turn the stirrer on. Adjust to a rate sufficient to form a vortex. Be sure the Karl-Fisher reagent has been titred and titrator is in "KFR" mode. Start the titration procedure to condition the solvent.

Press "Start" again to get a prompt for sample size. Inject 0.1 mL of the sample into the reaction vessel and replace cap. When injecting, be certain the sample falls into the solvent, not onto the vessel wall.

15. Return the 1 mL syringe to the 10 mL cylinder and note the weight in the lab book. Calculate the weight difference and enter this value into the Karl-Fisher titrator. Press "Enter" to begin the titration.

16. At the end of the titration, note the % Water Content.

17. Perform 3 titrations per sample.

18. Clean the bottles and separatory funnels with dichloromethane for next use.

Mass of mousse used at the various water to oil ratios and their corresponding demulsifier volumes.					
Ratio (WOR)	Oil Volume	Mousse Volume	Mass	Demulsifier Volume	
				(mL)	
	(mL)	(mL)	(g)	1:10 D/O	1:1000 D/O
47	17	85	84.6	1700	17
62.5	12.8	64	63.7	1280	12.8
125	6.4	32	31.8	640	6.4
250	3.2	16	15.9	320	3.2
500	1.6	8	8	160	1.6
Volume of demulsifier required for given ratios of demulsifier to oil using 85 mL of mousse.					
Ratio D/O	Demulsifier Volume				
1 to 1	17	mL			
1 to 5	3.4	mL			
1 to 10	1.7	mL			
1 to 12.5	1.36	mL			
1 to 20	850	μL			
1 to 25	680	μL			
1 to 50	340	μL			
1 to 100	170	μL			
1 to 200	85	μL			
500	34	μL			
1000	17	μL			
5000	3	μL			

Table 1 Results of Testing the "Demoussifier" Using Method Five

TESTS OF THE EMULSION BREAKER		
Ratio D/O	Viscosity (centipoise)	Viscosity Average
1:50	23.2	27.3
	25.2	
	31.6	
	29.0	
1:66.7	38.8	66.9
	76.4	
	46.1	
	106.3	
1:100	964.5	971.1
	974.4	
	1178.3	
	767.3	
1:250	494.0	376.9
	359.9	
	250.8	
	250.7	
	626.6	
	524.6	
1:500	132.1	494.4
	423.4	
	463.5	
	330.7	
	852.1	
	628.7	
1:750	267.9	2344.6
	2964.0	
	3485.8	
	1070.9	
	983.0	
	3451.8	
	4193.5	
	1309.8	
1:1000	1298.0	440.4
	300.0	
	534.4	
	492.5	
1:1500	453.8	3222.0
	421.2	
	2836.0	
	2914.0	
	3168.0	
	3417.3	
	3748.0	
	2862.5	

SECOND ROUND TESTS		
Ratio (D/O)	Viscosity (centipoise)	Viscosity Average
1:50	120.8	128.1
	122.2	
	65.2	
	204.1	
1:66.7	42.6	71.1
	81.4	
	80.3	
	86.5	
1:100	64.9	130.1
	87.3	
	203.1	
	89.0	
1:250	140.9	258.2
	199.4	
	435.1	
	200.3	
1:500	197.9	1126.9
	554.9	
	1176.3	
	1374.8	
1:750	1401.8	3271.9
	3128.2	
	1808.4	
	4059.9	
1:1000	4091.0	2778.5
	3525.0	
	2491.4	
	2589.4	
1:1500	2508.3	3735.4
	3562.5	
	3735.4	

Tests On The Emulsion		
Ratio (D/O)	Viscosity (centipoise)	Viscosity Average
Mousse (blender)	3244.3	3350.6
	3427.0	
	3380.3	
Mousse (butter churn)	3606.5	3389.9
	3173.3	
100% Broken Emulsion	250.7	383.5
	626.6	
	524.6	
	132.1	

Table 2 Data Using Method 6 - Lighter Mousse

Heavier Mousse

Ratio (D/O)	Viscosity (Pas)	Temp. C	Frequency (Hertz)	Average Viscosity	Water Content	Avg. H2O Content	Ratio (D/O)	Viscosity (Pas)	Temp. C	Frequency (Hertz)	Average Viscosity	Water Liberated	Avg. H2O Liberated	Water Content
Mousse	11.970	23.7	0.28				Mousse	18.000	23.9	0.34				
	10.460	22.7	0.33					17.330	21.1	0.34				
	9.332	23.8	0.35					16.730	22.9	0.28				
	14.240	22.6	0.31					19.370	21.2	0.27				
	12.980	22.1	0.37	11.786	80.66	80.66		20.360	23.9	0.33				
Blank	11.380	23.7	0.32					18.280	21.4	0.38				
Run	10.250	22.2	0.33					14.260	21.4	0.37				
	11.650	23.4	0.27		79.61			21.150	22.1	0.30	18.435			81.98
1:50	10.590	23.1	0.31	10.968	79.48	79.55		17.470	24.1	0.37		6.6		79.72
	0.187	24.4	0.33					23.650	22.0	0.30		6.3		
	0.332	19.9	0.34					23.010	23.5	0.33		8.0		
	0.088	24.6	0.33					24.090	21.0	0.31	22.055	8.1	7.3	82.85
	0.215	21.1	0.33	0.206				0.304	23.8	0.34				81.97
1:100	0.238	23.0	0.34					2.722	20.7	0.38				
	0.313	19.5	0.33					0.448	24.7	0.34	0.036	55.8		
	0.319	20.9	0.33	0.284				1.185	24.7	0.37		47.7		52.34
1:250	0.366	25.2	0.34					0.174	24.3	0.33		59.8		62.07
	0.590	20.8	0.34					0.131	20.5	0.33	0.827	58.0	55.3	41.94
	0.442	24.3	0.34					2.899	24.5	0.32		44.8		37.49
	0.466	20.7	0.35	0.466				5.186	21.2	0.34		42.2		
1:500	0.749	21.4	0.35					0.720	23.9	0.34		49.9		
	0.899	17.1	0.36					1.234	20.4	0.34		49.3		68.58
	0.795	18.4	0.36					0.693	24.0	0.34		38.2		63.51
	0.985	15.6	0.32	0.857				2.939	21.0	0.40	0.564	35.2	43.3	55.40
1:1000	1.307	18.5	0.33					1.189	24.0	0.34				66.36
	1.279	17.2	0.35					2.271	24.6	0.39				71.42
	1.404	17.6	0.33					0.621	24.7	0.34				70.92
	2.009	14.6	0.39	1.500				1.973	21.3	0.39	3.561	42.1		67.96
1:1500	1.486	23.8	0.33					7.228	24.9	0.33		40.8	41.4	67.38
	1.646	24.5	0.34					9.409	22.4	0.29		24.6		
	1.711	23.1	0.31					10.780	24.9	0.32		22.9		
	1.472	22.9	0.32	1.579				11.070	22.1	0.31	5.305	20.0	23.0	74.94
1:2000	1.760	24.0	0.39		68.15			19.250	23.0	0.25		12.6		76.85
	1.818	23.6	0.37		73.50			12.900	20.4	0.35		13.9		
1:3000	2.433	22.2	0.39	1.866	75.94	73.13		18.290	20.5	0.27		14.7		80.00
	2.272	25.0	0.31		61.50			14.520	20.4	0.31	8.526	15.5	14.2	78.82
	2.540	22.5	0.35		75.52			17.290	24.0	0.31		12.6		
	2.438	24.6	0.38		77.12			15.830	21.3	0.33		10.4		
	2.404	22.3	0.33	2.414	72.22	74.67		19.100	23.6	0.30		12.3		
1:4000	2.466	23.8	0.49					16.600	23.6	0.31	8.861	11.3	11.7	79.86
	2.630	21.8	0.38					19.860	23.7	0.26		6.5		80.10
	2.683	24.3	0.40		74.26			15.490	22.2	0.37		5.8		
1:5000	2.769	24.5	0.37	2.637	76.38	75.32		15.960	23.2	0.35		6.4		
	3.227	23.4	0.41					15.960	21.8	0.35	9.612	6.3	6.3	77.46
	2.904	24.2	0.36					18.170	24.5	0.30		7.6		77.98
	3.808	21.9	0.38		75.09			19.120	22.5	0.29		6.0		
1:6000	4.196	23.8	0.32	3.534	76.99	76.04		23.280	23.6	0.27		7.0		
	4.202	24.1	0.30					17.700	21.8	0.33	17.750	6.5	6.8	78.28
	3.741	22.7	0.40											77.34
	3.827	24.6	0.40		79.70									
	3.953	25.0	0.38	3.931	76.82	78.26								
1:7000	4.869	23.5	0.43											
	4.545	24.2	0.40											
	4.462	23.4	0.40		78.52									
1:8000	5.142	21.8	0.42	4.755	78.77	78.65								
	5.088	24.3	0.42											
	5.271	21.7	0.42											
	4.888	24.4	0.39		78.03									
1:9000	5.853	21.9	0.41	5.275	79.45	78.74								
	6.025	23.9	0.45											
	6.315	22.6	0.41											
	6.474	24.5	0.41		79.61									
1:10000	6.770	21.3	0.44	6.396	78.98	79.30								
	6.264	24.2	0.40											
	6.121	21.6	0.43											
	5.690	23.9	0.40		78.29									
	6.607	20.9	0.41	6.171	79.09	78.69								

Table 3 Results Using Method 6 - Alcopol and Direct Water Placement

Ratio (D/O)	Viscosity (Pas)	Temp. (Celcius)	Frequency (Hertz)	Average Viscosity	Standard Deviation	Water Content	Avg. H2O Content
Mousse	16.120	22.9	0.30	18.684	3.123	81.86 81.52	81.69
	15.020	20.9	0.34				
	21.150	22.0	0.29				
	22.720	21.9	0.26				
Blank Run	16.720	24.8	0.34	18.26	1.1	80.31 80.49	80.4
	19.160	21.6	0.32				
	18.200	24.0	0.35				
	18.940	22.1	0.39				
1:50	0.033	25.1	1.04	0.036	0.003	5.16 3.29	4.23
	0.039	22.4	1.76				
	0.037	20.8	1.04				
	0.119	23.0	0.33				
1:500	0.093	24.0	0.33	0.564	0.793	16.08 15.6	15.84
	1.479	19.7	0.35				
	1.836	24.4	0.32				
	1.837	27.1	0.37				
1:750	3.436	29.3	0.41	2.624	0.91	62.04 60.9	61.47
	2.632	23.6	0.40				
	3.050	20.5	0.33				
	3.439	23.8	0.29				
1:1000	5.121	20.9	0.29	3.561	1.091	66.6 69.07	67.84
	3.750	24.7	0.41				
	4.919	21.8	0.34				
	5.443	24.2	0.41				
1:2000	7.107	21.0	0.46	5.305	1.39	75.48 76.57	76.03
	7.842	24.7	0.27				
	10.500	22.7	0.29				
	8.695	23.8	0.32				
1:3000	7.569	22.6	0.32	8.526	1.09	77.86 77.68	77.76
	6.613	21.6	0.42				
	9.180	23.4	0.34				
	10.790	21.6	0.32				
1:5000	9.128	23.6	0.34	8.861	2.11	78.93 78.61	78.77
	10.760	21.8	0.31				
	10.160	24.1	0.27				
	8.398	23.9	0.35				
1:7000	12.140	22.4	0.31	9.612	1.05	79.61 77.33	78.47
	8.986	22.6	0.32				
	14.700	22.5	0.26				
	16.450	23.8	0.38				
1:9000	19.110	21.1	0.28	13.36	3.36	79.46 77.59	78.53
	16.340	24.5	0.35				
	19.100	22.1	0.33				
1:11000				17.75	1.57	80.56 81.37	81.01

Results for Demoussifier Applied Directly to The Water

Ratio (D/O)	Viscosity (Pas)	Temp. (Celcius)	Frequency (Hertz)	Average Viscosity	Water Liberated	Avg. H2O Liberated	Water Content	Avg. H2O Content
Mousse	18.000	23.9	0.34	18.435	56.8 57.3 57.8 50.8	55.7	78.99	79.42 79.21
	14.260	21.4	0.37					
	21.150	22.1	0.30					
	0.259	24.0	0.35					
1:50	0.861	22.7	0.38	0.406	48.1 39.2 38.7 23.0	41.4	64.27 67.28	52.40
	0.254	23.8	0.36					
	0.250	21.8	0.35					
	0.428	24.3	0.34					
1:500	3.939	23.8	0.29	2.104	19.4 17.7 15.7 16.6	22.4	75.15 75.03	65.78
	2.305	21.3	0.36					
	12.620	23.6	1.73					
	14.810	21.8	2.18					
1:2000	10.890	24.3	1.69	12.775	12.1 12.4	12.3	74.75 74.46	74.61
	12.780	21.3	1.68					
	21.970	24.7	0.25					
	14.100	24.7	1.80					
1:5000	16.140	22.4	2.04	19.333	19.02		76.58 77.14	75.09
	17.940	25.1	0.25					
	20.100	23.6	0.28					
1:7000				19.02			76.86	

Table 4 Tests of Shaking Times Using The Burrell Shaker

Values shown are Water Content After Treatment

Emulsion Breaker - "Demoussifier"						Emulsion Breaker - Aicopoi			
Ratio (D/O)	TIME (Hours)					Ratio (D/O)	TIME (Hours)		
	0.50	1	2	3	4		0.50	1	2
1 to 10	30.57	31.17	26.34	16.16	24.74	1 to 1	28.86		28.88
	51.65	49.98	21.20	18.32	14.28		30.34		29.03
1 to 50	61.54	57.89	44.55	25.00	42.50	1 to 5	46.88		35.79
	62.09	47.13	49.95	27.64	40.32		34.00		18.57
1 to 100	58.55	53.11	56.84	50.93	47.02	1 to 10	51.16	16.70	7.00
	63.71	58.06	60.51	48.79	50.22		50.50	14.26	6.85
	62.67	55.77	47.61			1 to 12.5	9.12		
	54.40	53.38	51.50			1 to 25	19.50		
		55.79					7.34		
1 to 200	70.57	58.25	55.37	45.00	60.74	1 to 50	12.81	1.74	4.88
	69.63	61.02	50.19	44.85	58.86		17.76	2.47	4.33
			57.47			1 to 100	32.10	10.92	4.86
			55.38				51.59	6.59	4.66
			61.65				36.02		11.63
1 to 500			56.02						12.18
	71.32	64.35	60.91						7.82
	71.48	65.13	56.98						5.28
			37.28			1 to 200	11.36	5.26	2.20
			49.55				50.04	11.16	4.48
1 to 1000	68.09	69.70	65.28	62.37	67.21		45.46		
	69.38	69.26	61.22	66.49	68.45	1 to 500	57.67	54.04	16.66
				69.13			45.57	51.94	3.50
				64.84		1 to 1000	50.96	70.56	68.01
							59.09	66.28	56.90
						1 to 5000	78.34		78.23
							80.68		76.84

Table 5

Tests of Shaking Times Using The Turbula Mixer

"Demoussifier"

All Data are Water Content After Treatment

D/O Ratio	Gear	Time (Hours)		
		0.50	1	2
1 to 10	3		35.95	34.12
			48.74	26.41
	4			30.92
		48.46	35.78	6.04
		45.56	33.34	2.46
1 to 50	3	43.23	24.21	16.36
		46.55	33.17	
			33.30	
		66.46	61.79	56.75
		69.94	66.25	54.24
	4		62.85	56.26
			59.12	47.40
		50.31	60.86	54.25
		56.10	63.39	53.32
		33.12	59.37	37.72
1 to 100	3	32.04	58.45	34.08
		71.69	73.71	69.38
		73.24	69.68	53.13
		73.21	72.17	63.67
		72.70	72.90	62.81
	4	73.25		
		69.27	47.10	29.52
		59.60	52.13	48.00
		60.50	48.48	48.51
		56.63	47.32	55.99
	5	62.36	45.18	
			51.47	
		40.23	34.73	34.70
		68.00	40.37	43.59
		51.79	40.27	52.79
1 to 200	3	48.77	47.11	40.77
		48.60	41.85	41.91
		48.09		43.99
	4			
		70.93	65.53	63.44
		71.19	66.64	69.49
		70.49	64.78	72.28
	4	71.82	67.06	71.14
		71.08	70.93	59.12
			66.60	
		65.98	57.55	48.22
	5	62.93	58.33	57.82
		68.25	53.93	56.67
		64.10	61.08	60.66
		73.66		52.13
1 to 500	3			
		76.42	71.73	58.39
		72.78	73.46	53.99
		73.71	74.03	55.78
		73.74	71.62	65.52
	4	70.28	71.76	54.10
		69.70	72.53	52.66
		70.20	64.68	52.94
		65.33	66.90	64.07
			60.42	62.10
1 to 1000	3			67.88
			62.06	51.03
			66.99	67.37
			67.82	71.06
			68.60	65.51
	4		68.22	66.38
		70.51	68.24	63.46
		72.99	68.18	61.55
		71.18	68.06	63.14
		72.38	71.21	62.54
1 to 5000	4	78.76	74.29	73.87
		79.52	74.83	73.91
		81.74	75.26	74.38
		76.35	75.02	74.80

Tests Using Demoussifier at
A Constant Ratio of 1:100

Gear	Time (Hours)		
	0.50	1.00	2.00
3	71.69	73.71	69.38
	73.24	69.68	53.13
	73.21	72.17	63.67
	72.70	72.90	62.81
	73.25		
4	69.27	47.10	29.52
	59.60	52.13	48.00
	60.50	48.48	48.51
	56.63	47.32	55.99
	62.36	45.18	
5		51.47	
	40.23	34.73	34.70
	68.00	40.37	43.59
	51.79	40.27	52.79
	48.77	47.11	40.77
	48.60	41.85	41.91
	48.09		43.99

Tests Using Alcopol

Ratio D/O	TIME (Hours)	
	1	2
1 to 5	22.72	27.61
	32.84	14.37
1 to 10	12.23	4.13
	7.45	6.64
1 to 12.5	6.00	10.95
	20.93	7.44
1 to 25	12.58	3.31
	5.44	4.90
1 to 50	4.62	4.82
	2.17	3.23
1 to 100	15.94	18.60
	2.64	11.89
1 to 200		15.36
	4.82	3.18
1 to 500	3.01	2.54
	7.94	10.46
1 to 1000	14.21	5.70
	71.64	62.58
1 to 5000	68.17	64.32
	75.45	76.78
	77.99	74.49

Table 6 Effect of Settling Time

Settling Time (minutes)	Ratio (Demulsifier to Oil)		
	1 to 50	1 to 100	1 to 1000
10	3.46	5.81	65.89
	6.22	3.00	68.85
30	3.47	3.21	63.10
	2.14	4.68	65.93
60	4.44	2.44	64.19
	4.28	3.26	66.72
120	2.54	4.27	64.23
	3.58	3.52	67.26

All Data
Are
Water
Content
In %

Table 7 Effect of Oil-To-Water Ratio
1:1000 Demoussifier to oil ratio

Ratio (WOR)	Time (hours)	Ratio	
		1 to 10	1 to 1000
47	0.50	30.57	68.09
		51.65	69.38
	1	31.17	69.70
		49.98	69.26
	2	26.34	65.28
		21.20	61.22
62.5	0.50	45.06	68.58
		45.17	63.62
	1		66.99
			71.14
	2	30.57	61.61
		30.56	64.37
125	0.50	42.73	68.90
		36.84	69.57
	1	36.92	65.42
		40.27	66.96
	2	19.90	57.39
		29.37	61.70
250	0.50	46.47	31.04
		46.88	40.41
	1	74.18	70.78
		73.82	70.14
	2	16.30	55.65
		15.59	57.32
500	0.50	37.62	73.48
		42.94	74.16
	1	29.71	68.63
		55.33	72.66
	2	23.58	51.36
		18.33	50.77

Table 8 **Energy Study - Turbula and Alcopol**

Gear	RPM	Ratio	(D/O)
		1:100	1:1000
1	20	26.68	69.78
		8.05	71.65
2	30	8.04	62.20
		7.42	65.80
3	42	15.90	50.94
		10.10	72.89
			71.06
4	62	18.60	62.58
		11.89	64.32
		15.36	60.80
			65.11
5	90	5.40	63.14
		4.66	63.15
		2.33	

Table 10 **Settling Time Effect
Burrell and Alcopol**

Time (minutes)	DOR 1 to 1000
0	72.42
	71.49
10	65.89
	68.85
20	68.56
30	63.10
	65.93
40	70.97
	72.21
	66.00
	71.39
50	69.44
	71.41
60	64.19
	66.72
80	68.04
	69.98
100	69.55
	72.12
120	64.23
	67.26

Table 9 **Shaking Time Study -Burrell and Demoussifier**

Ratio (D/O)	TIME (Hours)			
	3	4	5	8
1 to 10	16.16	24.74	9.80	10.71
	18.32	14.28	27.91	3.02
1 to 20	34.96	43.29	30.52	10.38
	37.30	49.11	27.01	
1 to 50	25.00	42.50	32.23	10.81
	27.64	40.32	44.25	57.58
1 to 100	50.93	47.02	35.07	45.77
	48.79	50.22	44.41	64.46
1 to 200	45.00	60.74	43.11	46.72
	44.85	58.86	44.71	39.29
1 to 500		53.79	54.09	55.02
		52.17	66.94	
			38.51	
1 to 1000	62.37	67.21	43.46	59.04
	66.49	68.45	41.97	
	69.13			
	64.84			

Table 10b
Settling Time -DOR 680

Time (hours)	DOR 1 to 680
0	48.40
1	49.52
2	32.01
24	31.54

Table 11 **Energy Study Results**
Turbula and Demoussifier

Gear	RPM	Ratio (D/O)	
		1 to 10	1 to 100
1	20	26.62	73.52
		49.97	74.25
		33.34	
2	30	35.76	65.50
		49.08	64.92
		11.89	
3	42	22.84	50.26
		17.91	50.24
4	62	4.67	35.45
		6.19	35.03
5	90	7.09	39.81
		1.79	14.59
			22.63

Table 12 **Results from No Energy Input**
Demoussifier

Ratio (DOR)	Time (Hours)	
	2	24
0	20657	20657
1 to 1000		10230
1 to 100	3254	3740
1 to 10	1951	1823

Measurements given in centipoise

Table 13 **Results of No Energy Input**
Alcopol

Time (hours)	Ratio (D/O)			
	1 to 10	1 to 100	1 to 500	1 to 1000
24	61.42	58.20		74.95
	58.69	63.67		76.51
2	78.36	66.71 *	77.79	79.72
	78.55	71.16 *	78.07	79.50
	76.64	76.47		
	75.44			

Table 14 **Results of No Energy Input**
Alcopol

Time (hours)	DOR	
	1 to 1000	
0	62.04	
4	49.55	
24	32.62	
48	29.46	

Table 15 **Effects of Water-to-Oil Ratio**

Ratio (WOR)	Ratio (Demulsifier to Oil)		
	1 to 10	1 to 100	1 to 1000
47	7.00	4.86	68.01
	6.85	4.66	56.90
		11.63	
62.5		12.18	
		7.82	
		5.28	
	4.55	3.07	69.05
125	4.53	5.44	69.09
	11.84	5.47	66.76
	4.73	5.14	62.94
200			65.83
		10.40	76.33
		17.66	75.46
250	4.39	11.62	66.70
	3.83	16.29	65.96
333.3		23.39	76.87
		20.62	75.46
400		33.38	76.31
		34.03	76.78
500	7.37	17.11	74.56
	2.45	31.96	76.06

all data except where noted are
water content in percent

Table 16 **Emulsion Stability Tests**
Blender and California Crude/ASMB Mix

Time (Days)	Approximate Water Content							
	10	20	30	40	50	60	70	80
0	13.56	25.58	35.16	44.11	54.04	61.35	71.74	79.73
1	13.68	25.40	35.56	44.47	54.10	61.75	72.36	79.31
2	14.54	26.01	35.72	44.76	54.47	61.93	71.77	78.45
3	14.83	25.69	35.98	43.59	54.42	61.19	71.74	78.04
4	13.64	25.45	35.59	44.05	54.46	61.30	71.96	78.98
5	14.24	24.86	35.43	45.40	54.80	61.49	71.87	77.97
6	13.40	25.52	35.25	43.55	54.55	60.35	70.76	79.62
7	13.45	25.06	34.50	44.79	55.21	60.20	71.20	77.10
Avg.	13.92	25.45	35.40	44.34	54.51	61.20	71.68	78.65
Std.Dev.	0.54	0.36	0.45	0.64	0.37	0.62	0.49	0.92

Table 17 **Stability of Emulsion Formed in Turbula Shaker**
California Crude/ASMB

Gear	RPM	Time (Hours)		
		1	2	3
1	20	54.38	78.99	85.19
		40.25	62.27*	57.62
2	30	69.58	63.86	65.62
		66.25	56.35*	75.11
3	42	66.39	70.52	71.16
		61.61	60.98	68.04
4	62	58.04	63.84	76.40
		68.32	73.34	77.76
5	90	60.13	75.23	72.48
		67.85	64.63	74.01
		72.80		

* = unstable before 5 days

Table 18 **Stability of Emulsion Formed in Turbula Shaker**
Iranian Heavy Crude

Gear	rpm	Time
		2 hours
1	20	86.42
		86.46
2	30	81.97*
		79.66
3	42	77.13
		75.56
4	62	76.01
		73.83
5	90	77.74
		70.53

* = unstable before 5 days

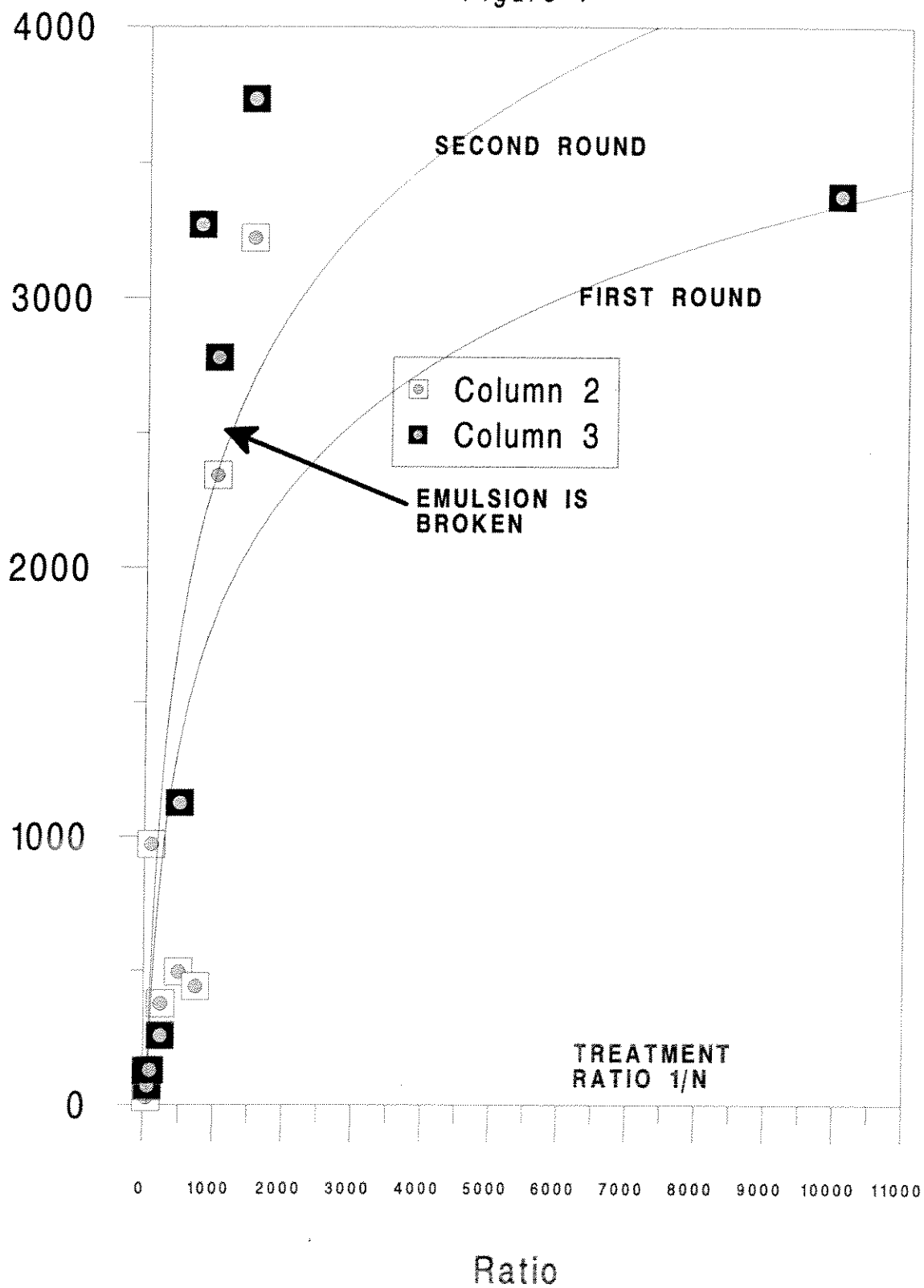
all data are water content in %

VISCOSITY VERSUS TREATMENT RATIO

TREATMENT OF EMULSION WITH DEMOUSSIFIER
- TESTING USING METHOD FIVE

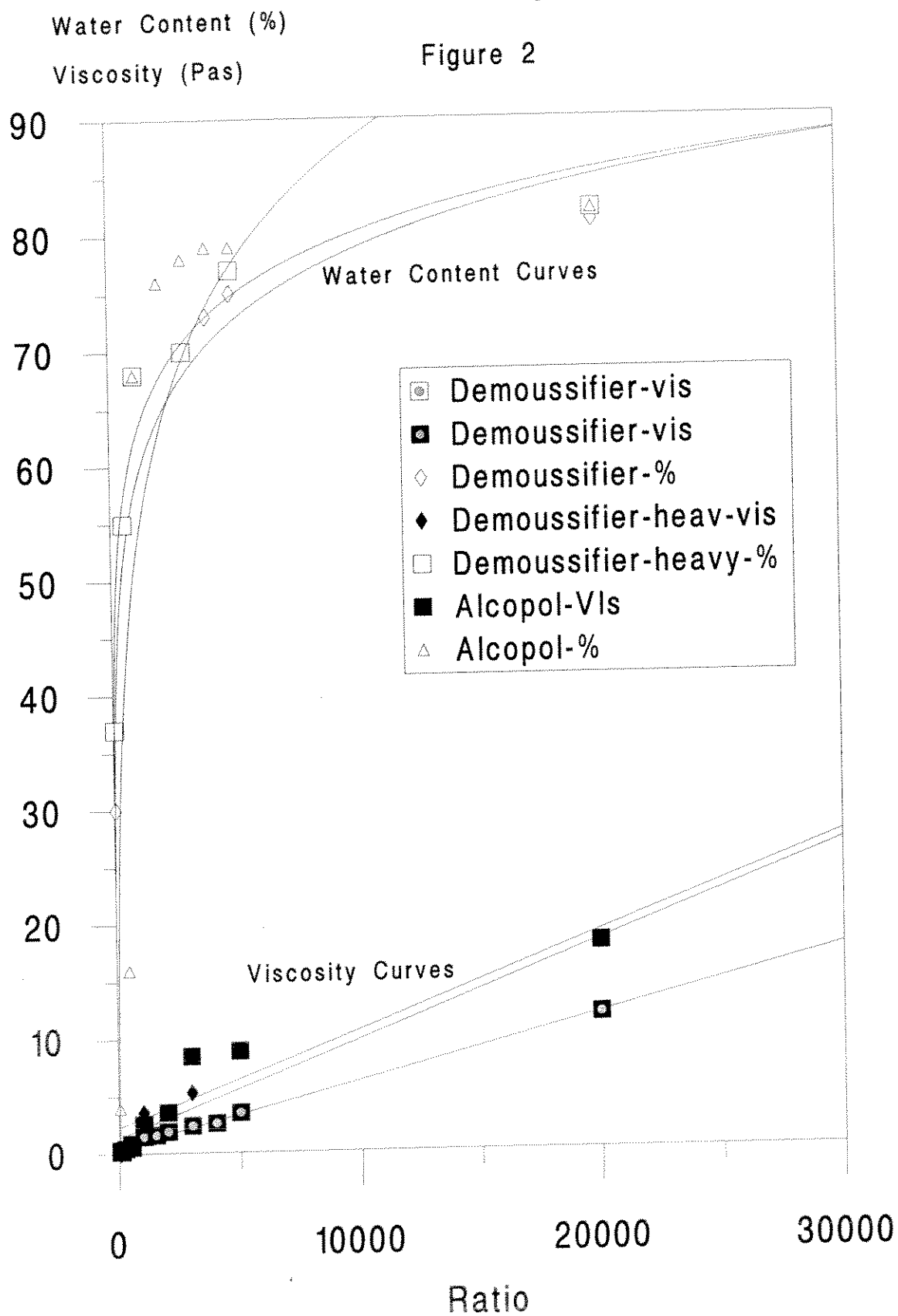
VISCOSITY (cP)

Figure 1



Test Results Using Demoussifier and Alcopol

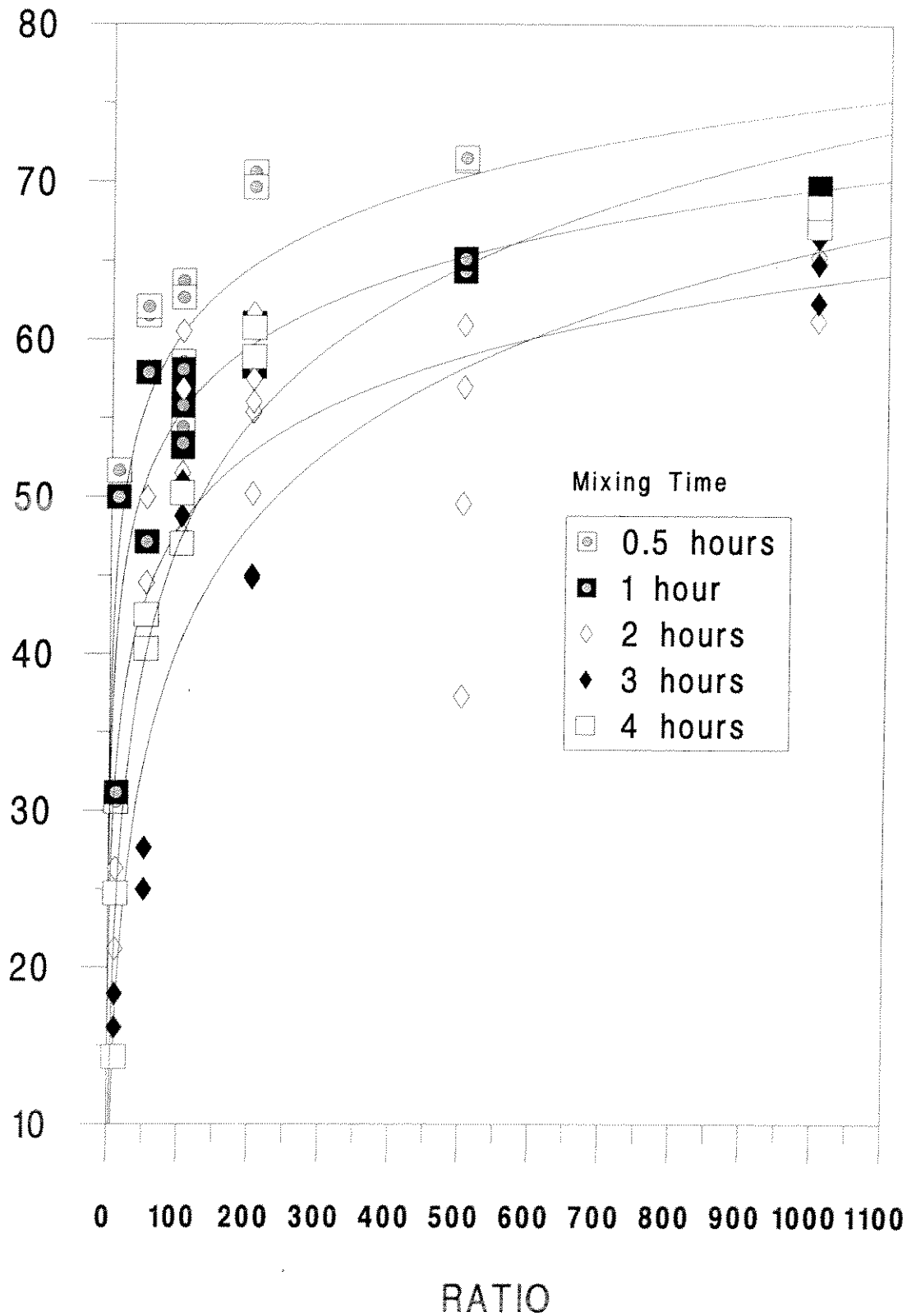
Figure 2



Shaking Time Study Burrell Shaker - "Demoussifier"

Water Content %

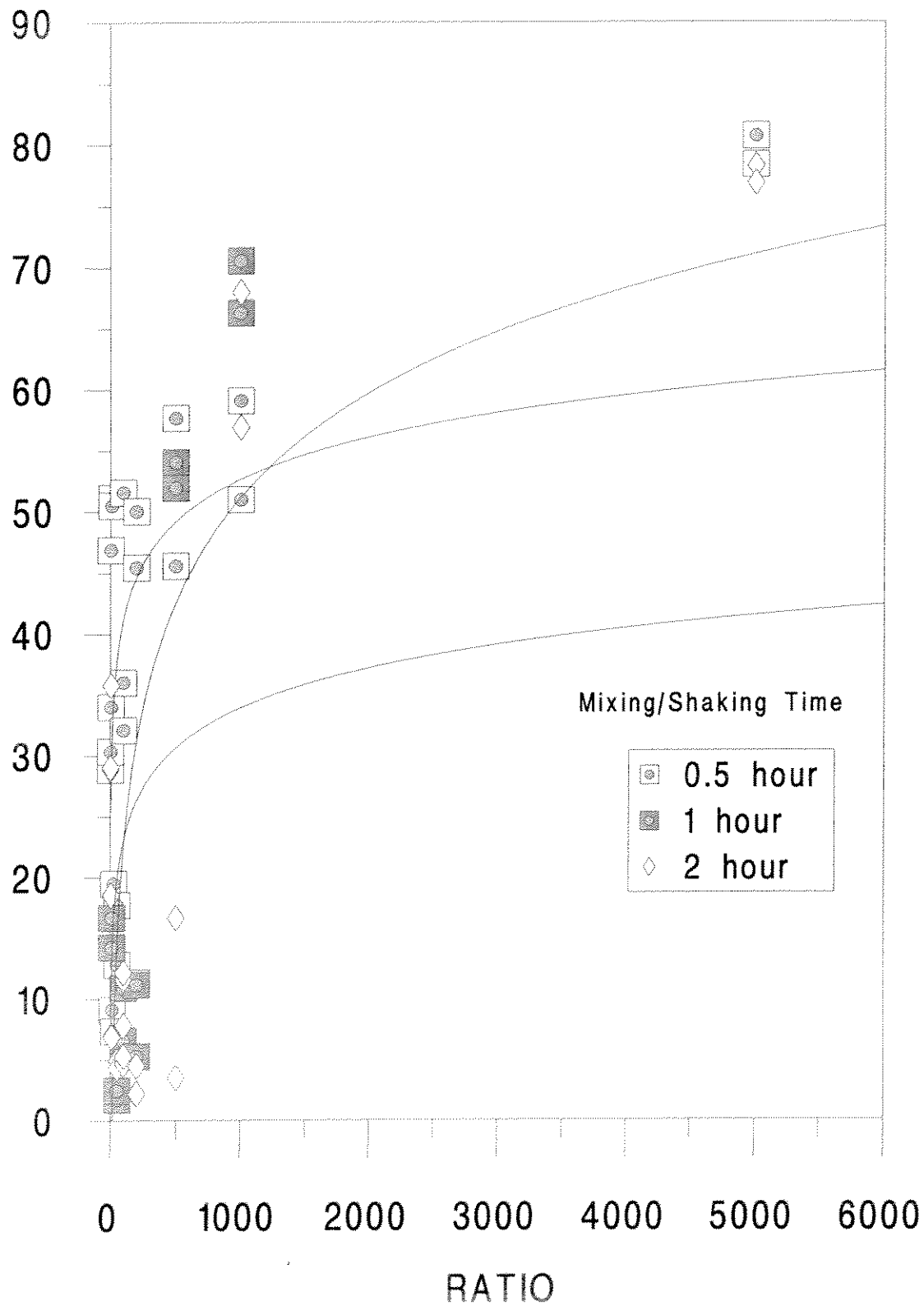
Figure 3



Shaking Time Study Burrell Shaker - Alcopol

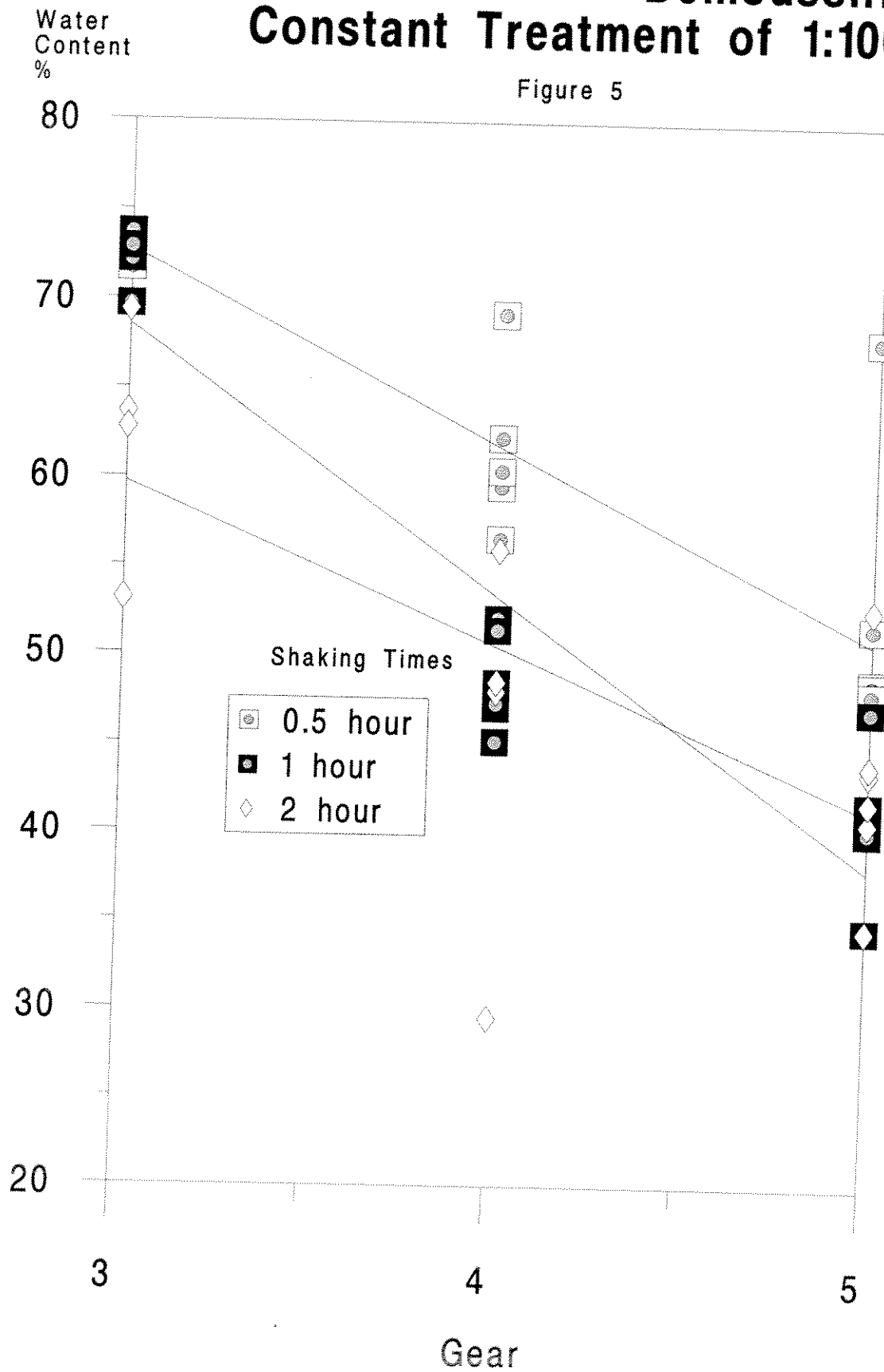
Water Content %

Figure 4



Shaking Time Study Turbula Shaker - Demoussifier Constant Treatment of 1:100

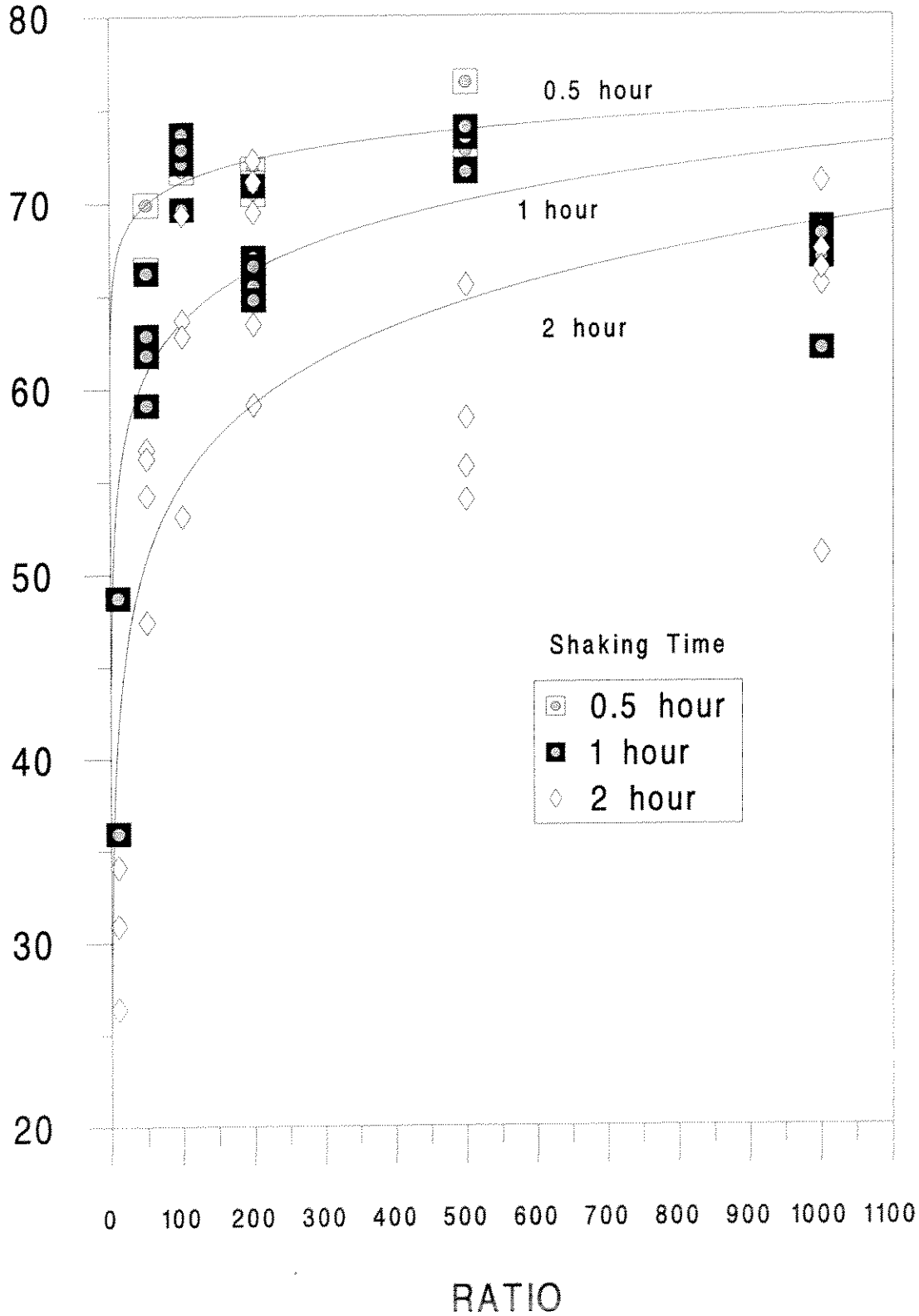
Figure 5



Shaking Time Study Turbula Shaker - Demoussifier Shaker at Gear Three

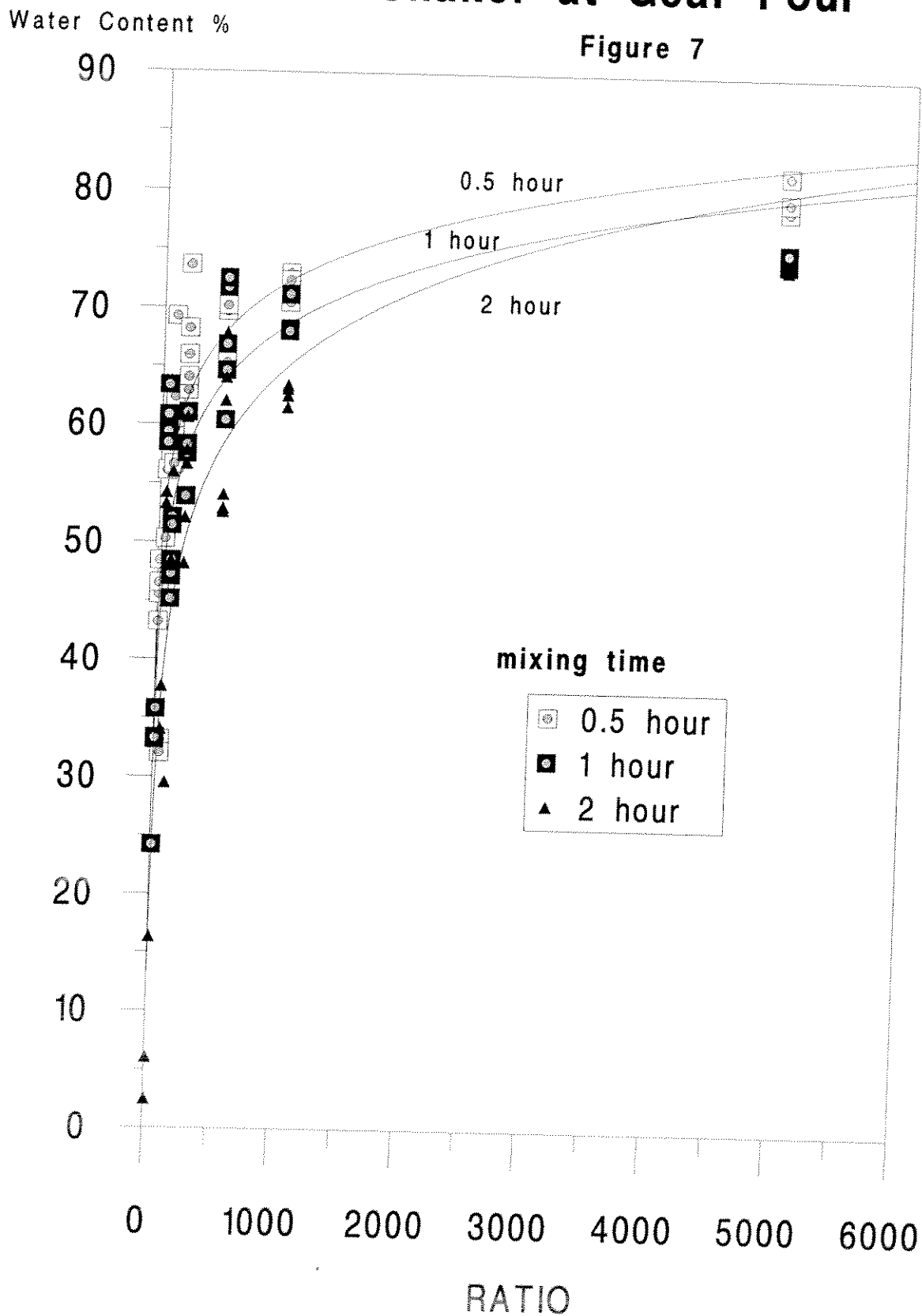
Water Content %

Figure 6



Shaking Time Study Turbula Shaker - Demoussifier Shaker at Gear Four

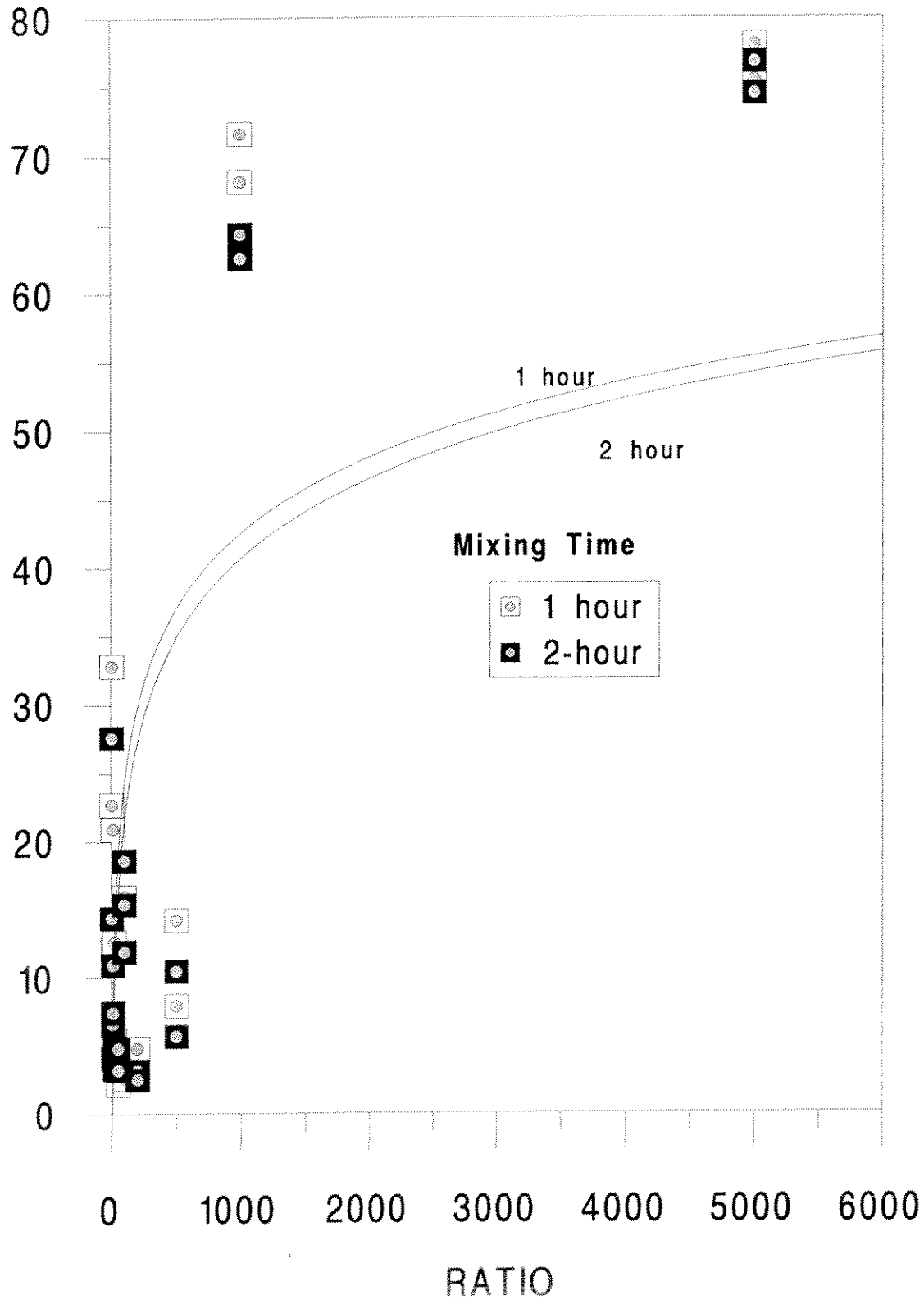
Figure 7



Shaking Time Study Turbula Shaker - Alcopol Shaker at Gear Four

Water Content %

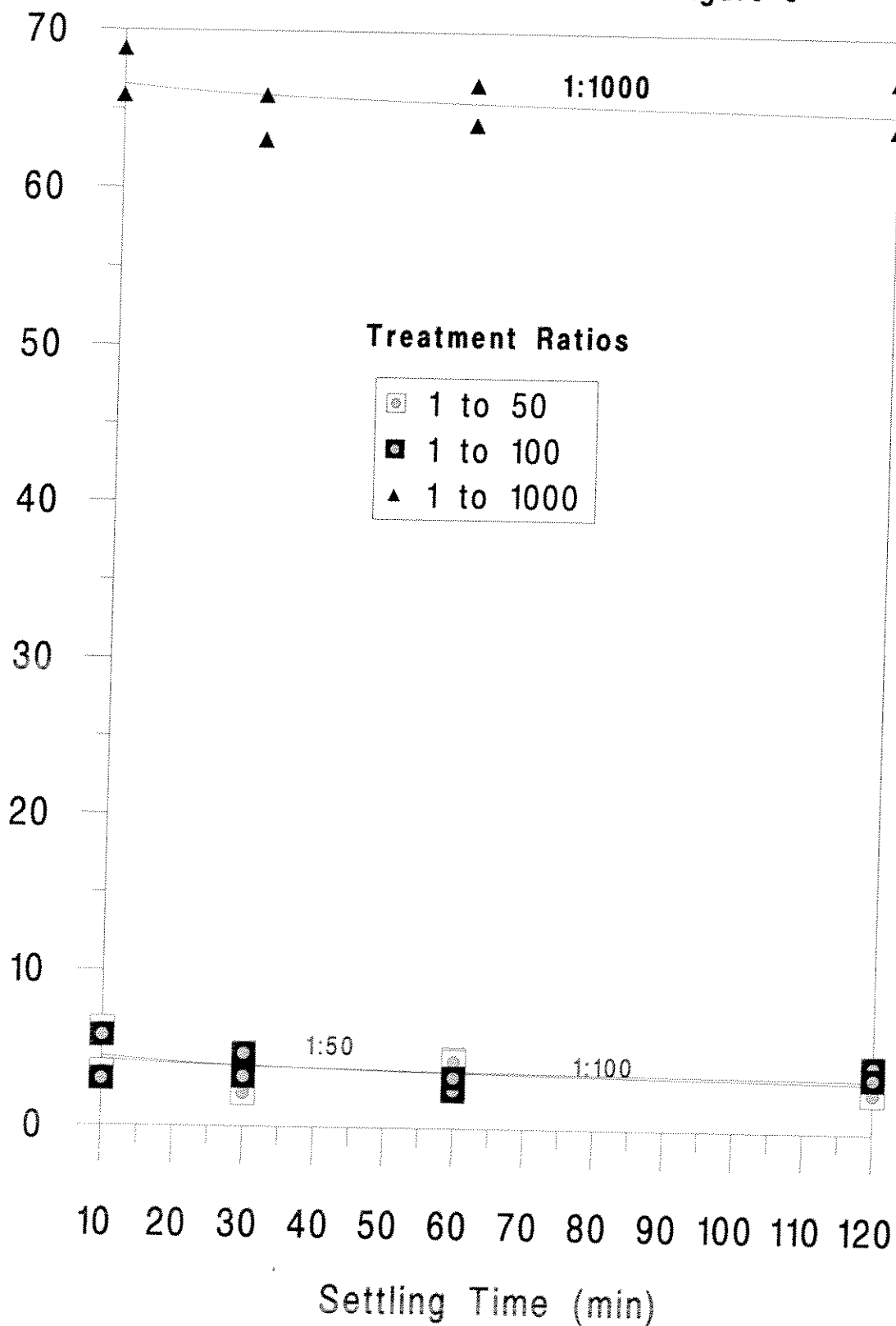
Figure 8



Effect of Settling Time Demoussifier in Burrell Shaker

Water Content %

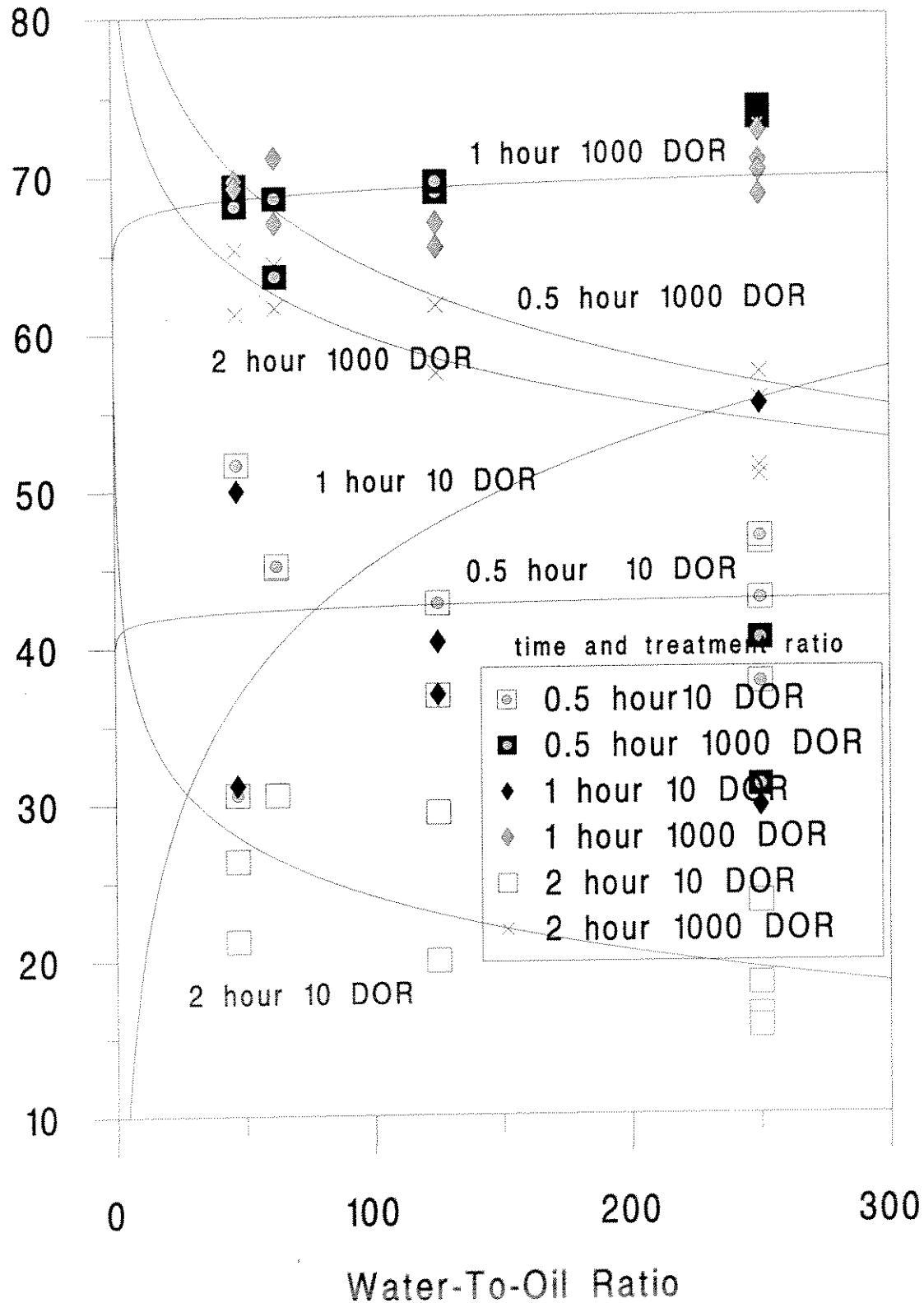
Figure 9



Studies on The Effect of Energy Burrell Shaker - Demoussifier

Water Content %

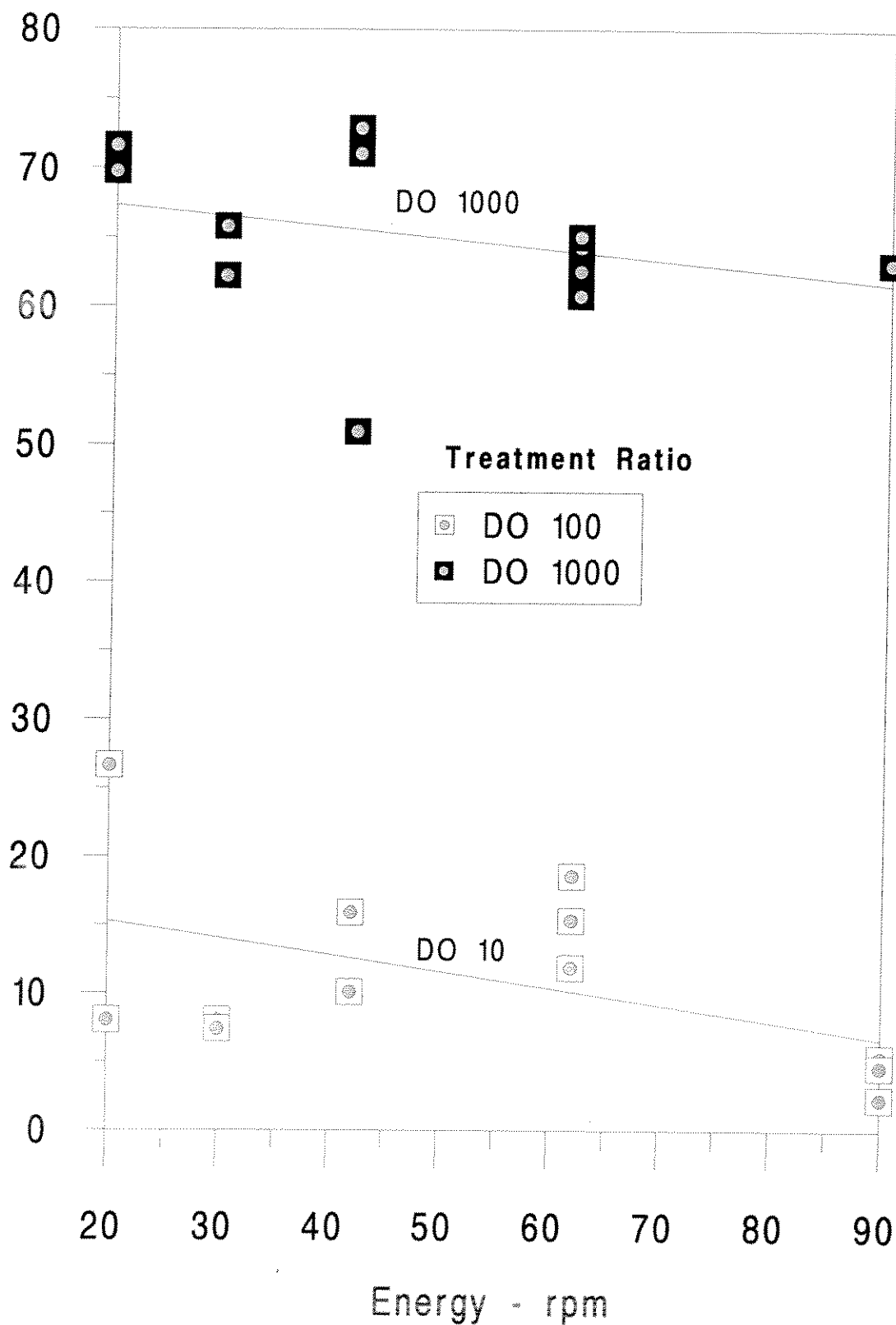
Figure 10



Effect of Energy Level Turbula and Alcopol

Water Content %

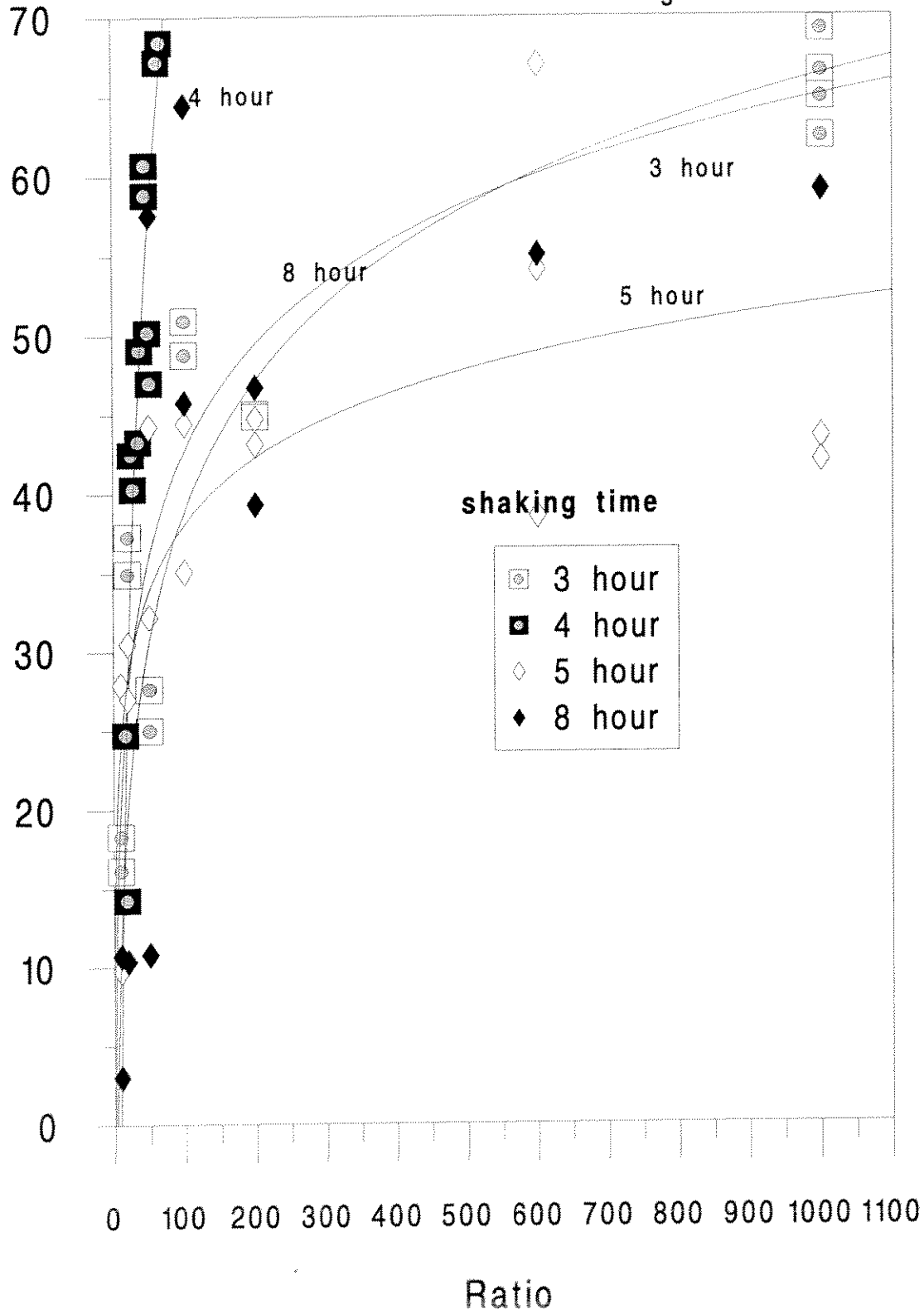
Figure 11



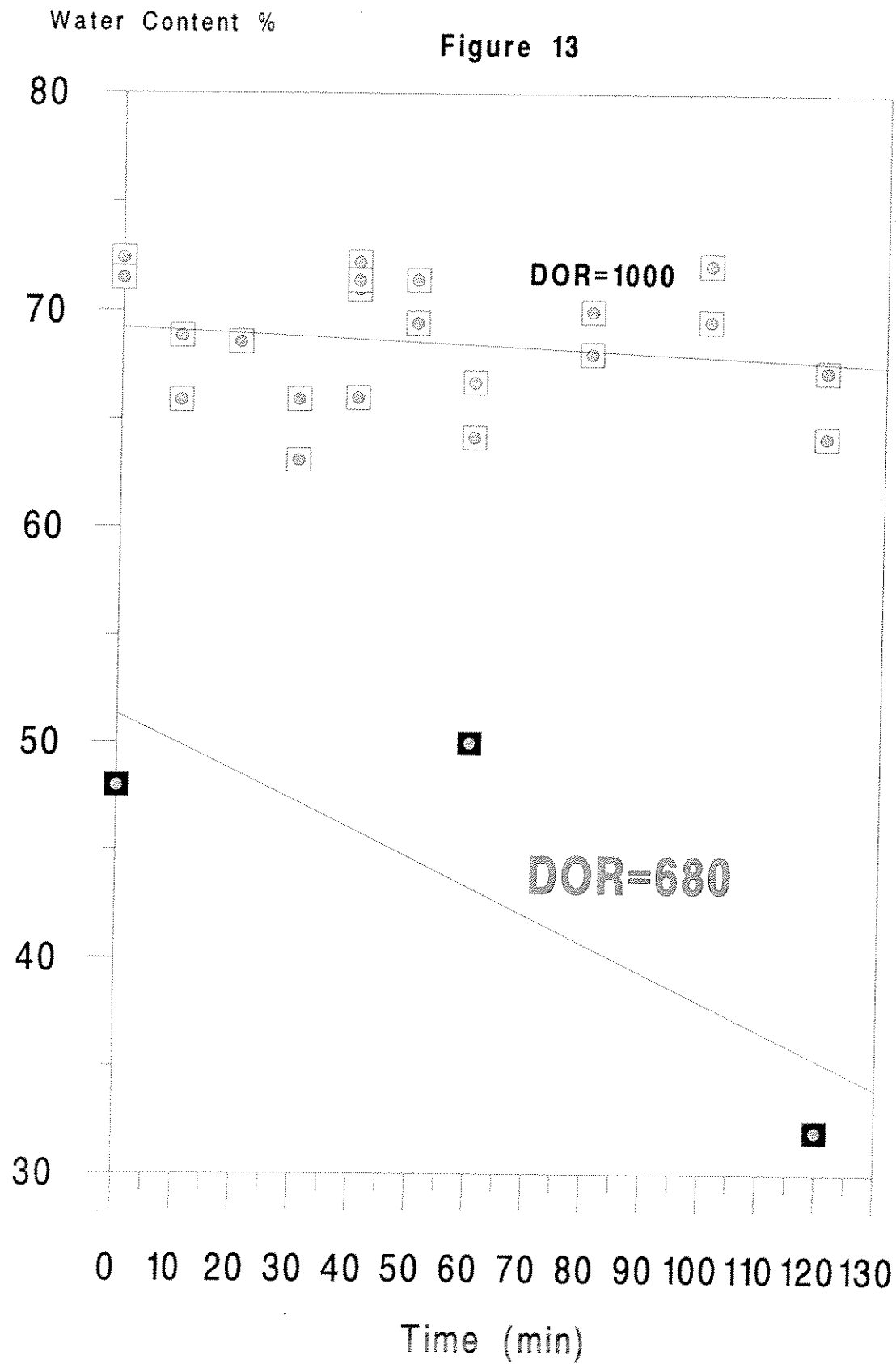
Shaking Time Study Burrell Shaker - Demoussifier

Water Content %

Figure 12



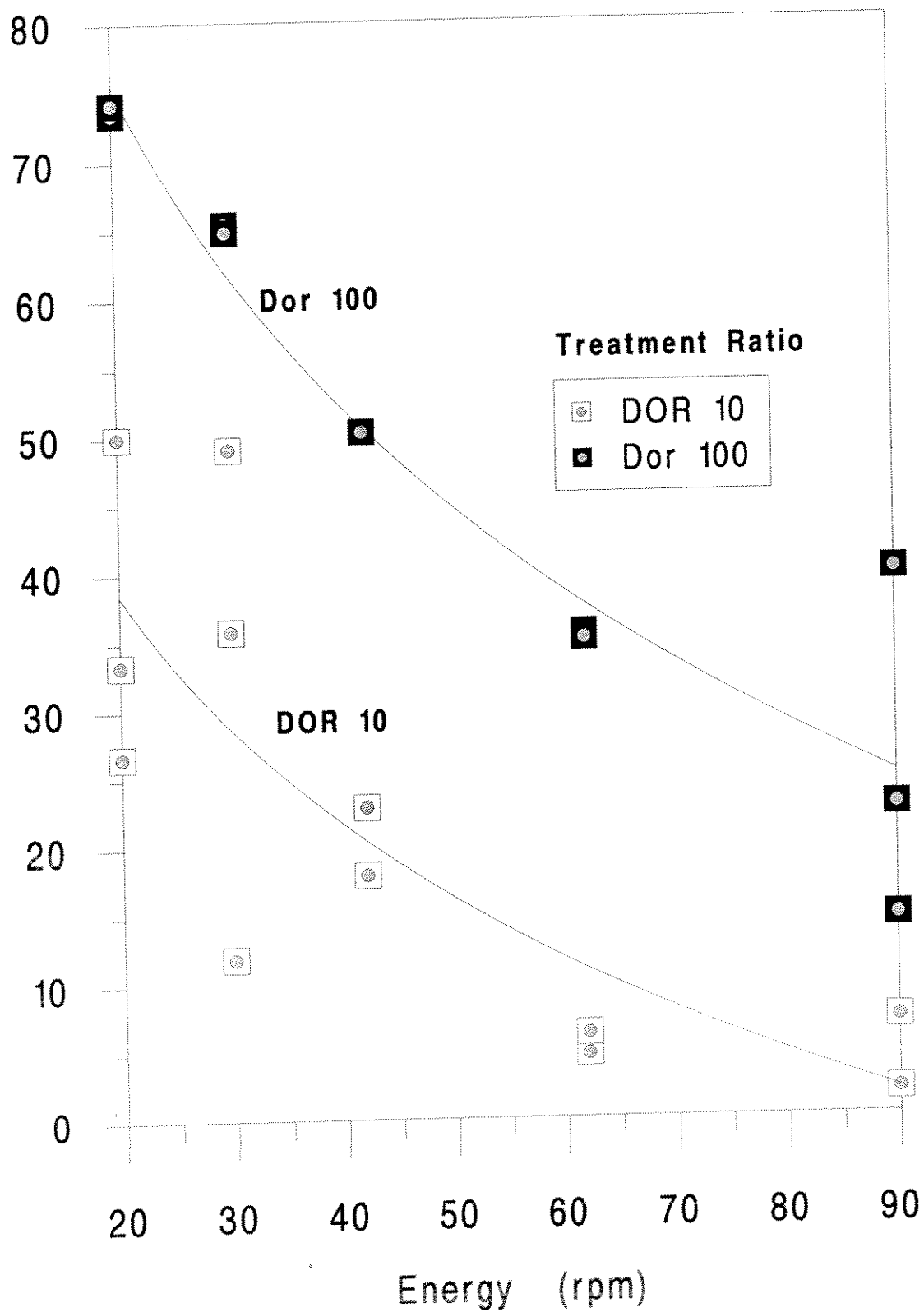
Effect of Settling Time Burrell Shaker - Alcopol



Effect of Energy Turbula and Demoussifier

Water Content %

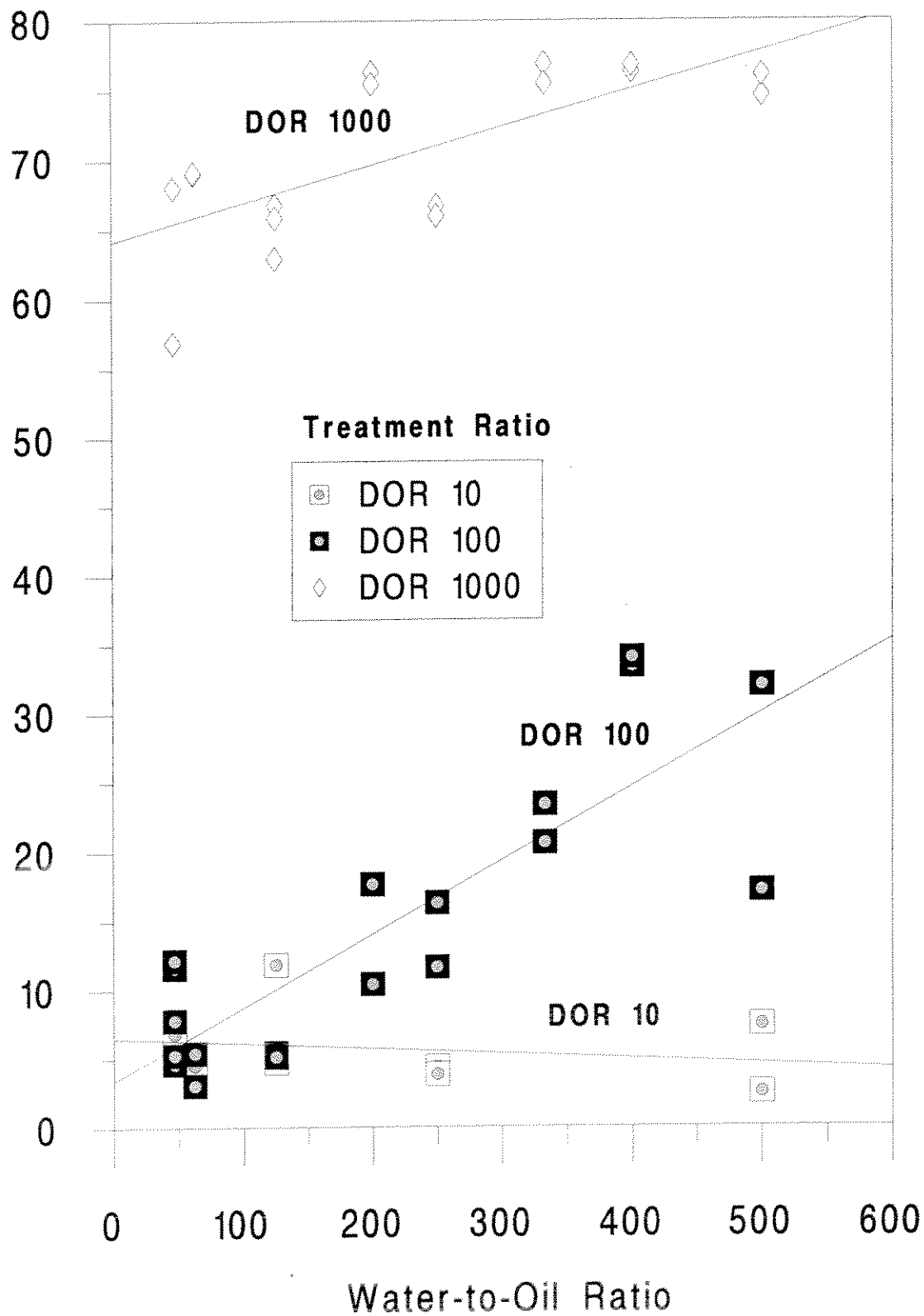
Figure 14



Effect of Water-to-Oil Ratio Burrell Shaker - Alcopol

Water Content

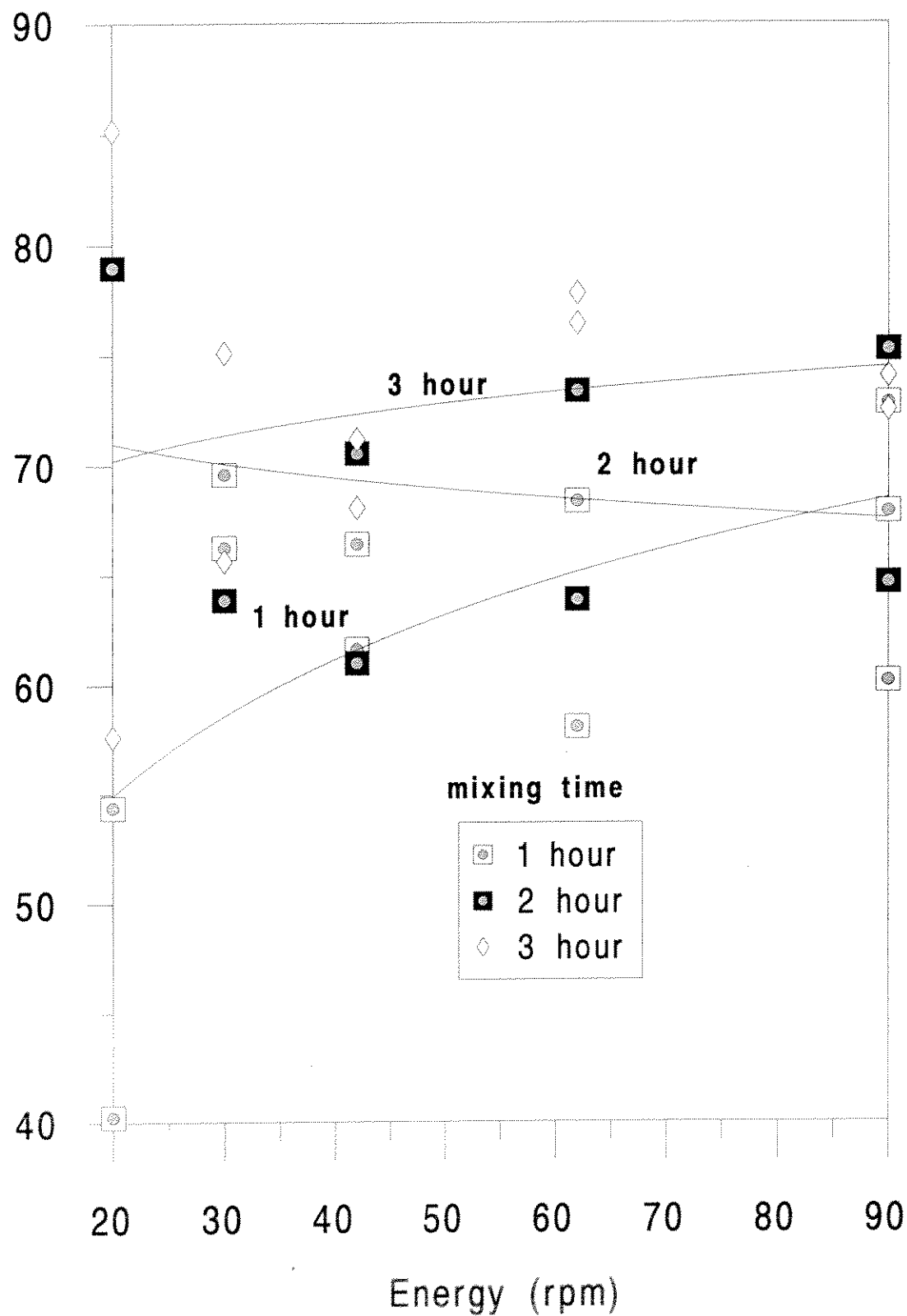
Figure 15



Emulsion Stability Turbula - Emulsion Mix

Water Content %

Figure 16



Stability of Emulsions

Turbula - Iranian Heavy Crude

Water Content %

Figure 17

